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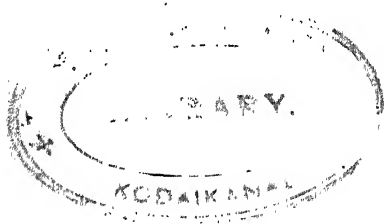
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Chemical Reactions *of the* Photographic Latent Image

VOLUME I

By E. R. BULLOCK

ILLUSTRATED



D. VAN NOSTRAND COMPANY
NEW YORK CITY

EASTMAN KODAK COMPANY
ROCHESTER, N. Y.

1927



MONOGRAPHS ON THE THEORY OF PHOTOGRAPHY

Edited by

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and

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Preface to the Series

The Research Laboratories of the Eastman Kodak Company were founded in 1913 for research work on photography and the processes of photographic manufacture.

The scientific results obtained in the Laboratories are published in various scientific and technical journals, but the work on the theory of photography is of so general a nature and occupies so large a part of the field that it has been thought wise to prepare a series of monographs, of which this volume is the sixth. In the course of the series it is hoped to cover the entire field of scientific photography, and make available to the general public material which at present is distributed through a wide range of journals. Each monograph is designed to be complete in itself and to cover not only the work done in the Laboratories but also that available in the literature of the subject.

Naturally a large portion of material in these monographs will be original work which has not been published previously, and all views expressed by authors of a monograph are not necessarily shared by other scientific workers in the Laboratories. The monographs are written by qualified specialists who are given liberal expression of their opinions. Each monograph is edited by the director of the Laboratories and by the active editor of the series.

Rochester, New York
November, 1927

Preface

A photographic sensitive layer is composed of crystals of silver halide. When affected by light, these crystals become developable, and in the developer they are reduced to an amorphous mass of silver.

Crystals which have undergone this change to light and have become developable may be said to constitute the latent image, or more specifically, the term 'latent image' may refer to the units of changed material which are supposed to occur upon the crystal; it is improbable that an exposed crystal of silver bromide is changed in its entirety; but it is assumed that some small portion of the crystal is changed and that these specks of changed material form a nucleus for development.

From the earliest days of photography, the nature of the change and the nature of the resulting material, generally referred to in photographic literature as the 'problem of the latent image,' have been the subject of investigation and speculation.

Even when they are of the same size, all silver halide grains are not equally sensitive to light. There is evidence that such grains have on their surface or enclosed in their mass specks of other material to which sensitiveness is largely due, and the nature of these sensitizing specks is a problem of interest, although the recent work of Dr. S. E. Sheppard on the sensitizing substance found in gelatin probably leads to a definite conclusion.

The nature of the latent image substance, therefore, and the nature of the sensitivity specks are two problems of fundamental interest in photographic theory.

There are several methods for investigation of these problems, and much light has recently been thrown on the nature of the latent image by quantitative study of exposure and development and especially by the statistical study of the developability of the separate crystal grains after exposure, a method which has been expanded by Dr. Svedberg, by workers of the British Photographic Research Laboratory, and by the staff of the Kodak Research Laboratories.

Much evidence as to the nature of the latent image and the sensitivity specks must, however, come from their reactions to chemical solutions, and in this monograph Mr. Bullock has collected information available in the photographic literature and has analyzed this material so far as possible, adding to it accounts of much original work on the effect of chemical solutions upon the latent image and on sensitivity. Although

his conclusions are tentative, publication of the material should be available to those who are engaged in work on the subject. Since the effect of different developers must throw light upon the nature of the latent image and perhaps on the process of development itself, Mr. Bullock has included a study of the effect of development upon threshold speed and, also, an account of many experiments made on the production of a latent image by other agencies than that of light, which effects are conveniently known by Dr. Clark's term 'pseudo-photographic.'

Thanks of the author are due to *Science et Industries Photographiques* for permission to include in this monograph much material that has been previously published in that journal.

C. E. K. MEES

Rochester, New York

November 30, 1927

Chemical Reactions of the Photographic Latent Image

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Chemical Reactions of the Photographic Latent Image

CHAPTER I

Literature Relating to the Action of Silver- Oxidizing Baths on Sensitivity and on the Latent Image

The present chapter summarizes the work which has been published relating to the action of certain oxidizing solutions on sensitivity and the latent image, that is, to the action of these solutions applied, respectively, before and after exposure. The solutions, not themselves necessarily dilute or at room temperatures for their action on the photographic sensitive materials, were defined as those of substances which, when in dilute aqueous solution and at room temperatures, are usually accepted as being capable of attacking silver and converting it quantitatively into a salt, or mixture of salts, of silver. Examples of such solutions are those of potassium permanganate with sulfuric acid, converting silver to silver sulfate; mercuric chloride, converting silver to a compound or mixture of silver chloride and mercurous chloride; bromic acid, converting silver to silver bromate and bromide; iodine in potassium iodide, converting silver to silver iodide; and potassium polysulfide, converting silver to silver sulfide. In view of the extreme slowness of the initial action of cold, dilute, pure nitric acid, it seemed appropriate to exclude this substance from the list of silver oxidizers considered, although nitrous acid, whose action, under similar conditions, is notably faster is included.

Shadbolt, in the *British Journal of Photography*,¹ writes: "That an actinic impression can be removed from a sensitive collodionized film we have not a shadow of a doubt; and, what is still more important, it can be removed from a sensitized collodio-albumenized plate, as we have proved by direct experiment. But this is to be accomplished, not by an iodide, but by iodine. If a sensitive plate that has been exposed to light be soaked for a short space of time in water containing a few drops of tincture of iodine, and then drained, washed, and dried, it will be found to have regained its former capacity of receiving an impression in the camera. Of this we are certain;

¹ G. Shadbolt: *Brit. J. Phot.* 8: 355. 1861 (Oct. 15).

but whether it receives an equally vivid impression in the same space of time for exposure we are not prepared to decide. One thing must be noted as of importance to success in this experiment, namely, that the iodized water shall not have been entirely decolorized, which is an indication that the amount of tincture of iodine added has not been quite sufficient: in that case the plate should be again soaked in a fresh quantity of water prepared as before." Since the tincture of iodine of the *British Pharmacopoeia* contained then as now not only iodine but also potassium iodide, Shadbolt's conclusion that iodine and not iodide is the effective agent in destroying a latent image in a collodion film and so rendering it again available for receiving a light-impression, does not logically follow from the experiment described. His conclusion, however, is strongly supported by later evidence and by the following quotation from Taylor² which shows that iodine, in the form of vapor, had long been known to destroy the latent image. "Curious things were done 'in the days of old' by a knowledge that iodic and kindred fumes would so discharge an impressed daguerreotype that no amount of exposure over the mercury would suffice to bring it out. I still remember the day when an amateur of considerable pretensions had invited three or four less successful brethren to spend a day with him, to see him operate, with the amiable intention of 'crowing' over them. It is still vividly before me how, time after time, he exposed—with no success—and I doubt not to his own profound amazement. The only cause he could assign was, that there must be electricity in the atmosphere, which prevented the possibility of a picture being taken! The real cause, however, was found to be that a young fellow present who was desirous that his boasting friend should, as he expressed it, 'have the starch taken out of him,' had slyly conveyed a small quantity of iodine into the camera, where, lurking unseen, it produced its baneful effects of throwing a 'wet blanket' over the too-confident operator." Presumably it was solid iodine and not tincture of iodine, that was employed, but in either case, iodine either as vapor or in solution would gain access to the sensitive film. The result may be interpreted either as a complete desensitization or as a complete destruction of the latent image.

Wardley³ makes the statement: "In the Daguerreotype process we certainly can destroy the image and restore sensitiveness at the same time; but *not* by means of an *alkaline iodide*, but by free *iodine* or *bromine*." Free iodine or bromine

² J. T. Taylor: *Brit. J. Phot.* 9: 44. 1862 (Feb. 1).

³ G. Wardley: *Brit. J. Phot.* 9: 15. 1862 (Jan. 1).

in actual contact with the respective silver halide diminishes the light-sensitivity of the latter either for direct printing-out or for physical development by means of mercury vapor or of a nascent silver solution. Under the conditions of sensitization and use of daguerreotype plates, however, any excess of free halogen could not exist permanently, for if condensed and loosely retained by the halide already formed, it would eventually disappear, if not by vaporization, at least slowly by combination with the silver of the metallic support. It is natural, therefore, that the diminution of sensitivity of silver iodide or bromide by the respective halogen should have passed unobserved in this process.

Carey Lea⁴ states that not only the latent image of a wet collodion plate but also one on pure silver iodide (iodized silver on glass mirror) is destroyed by the action of potassium iodide solution, dilute nitric acid, or mercuric nitrate solution. Reissig had previously stated that potassium iodide destroys the image in the former case but not in the latter. In the sense of this discussion, of the three solutions named by Carey Lea, only the mercuric nitrate is a silver-oxidizer, and in the light of present knowledge there is little doubt that mercuric nitrate is a destroyer of the latent image in any silver halide process. In these experiments it is possible that Reissig and Carey Lea, in testing for survival of latent image after treatment with the chemical under consideration, did not carry development to the point at which the non-appearance of a picture could fairly be interpreted as non-survival of the latent image.

Carey Lea finds also, for wet collodion and an iron-silver developer, that the interposition of development, or of development and fixation, after exposure and before treatment with mercuric nitrate, nitric acid, or similar solutions, allows the image to be regained by a second immersion in the same developer, that is, the visible image is removed by the mercuric nitrate and the latent image seems to remain. It is less probable that the original latent image survives and gives rise to the visible image in the second development, than that a new invisible image is produced in connection with the chemical reaction between the mercuric nitrate solution and the silver of the first developed image. This was suggested by the results of an attempted repetition of the experiments in this Laboratory, using gelatin (Eastman Slow Lantern) plates instead of collodion. In the absence of more definite knowledge, it may be surmised that the reaction is not entirely $\text{Ag} + \text{Hg}(\text{NO}_3)_2 = \text{AgNO}_3 + \text{HgNO}_3$, but to some extent $2\text{Ag} + \text{Hg}(\text{NO}_3)_2 = 2\text{AgNO}_3 + \text{Hg}$,

⁴ *Ausf. Handb. Phot.* II: 42. 1895; from *Phot. Archiv.* 133, 135. 1866.

under the conditions of the action of the mercuric nitrate on the first developed image,—the mercury element then serving as a nucleus for chemical development in the presence of silver halide, and for physical development in its absence.

In the *British Journal of Photography*⁵ it is stated, as the result of a series of experiments with collodion emulsion, that "in the case of an undeveloped film treated with alkaline chloride, bromide, or iodide, if thoroughly washed, so as to remove as far as possible all trace of the salt, an image may be subsequently developed, whereas a metallic haloid removes the image entirely." The "metallic haloid" used was cupric chloride or cupric bromide.

The prevention of fog in, or its removal from, collodion dry plates, is discussed by Abney in a communication⁶ to the Photographic (later the Royal Photographic) Society and in some supplementary remarks.⁷ While it may be asserted that a substance destroying fog will act as a preventive of fog, the converse is not necessarily true, and it is only the fog-destroyers, the more limited class, that can appropriately be considered in the present discussion. Abney shows experimentally that light-produced latent fog on collodio-bromide emulsion is completely destroyed by a cupric bromide, and "nearly entirely destroyed" by a ferric chloride solution, but scarcely affected by a solution of potassium bromide. He shows the fog-destroying action of bromine water, and also of a "solution of iodine in alcohol." In a description of some "further experiments undertaken with a view of ascertaining the cause of the fading away, by long keeping after exposure, of the undeveloped image impressed on (collodion) dry plates," Abney⁸ states that "films containing pure silver iodide and pure silver bromide after exposure under proper conditions were washed and treated with potassium bichromate, potassium permanganate, and chromic acid. With the first-named silver compound all were effective in destroying the image. With the last-named silver salt the two last oxidizing agents alone were effective, the permanganate requiring a longish application."*

⁵ On Metallic Chlorides and Bromides in Emulsions. *Brit. J. Phot.* **24**: 362. 1877 (Aug. 3).

⁶ W. de W. Abney: On Fog-Producing Emulsions, and on the Colour of Emulsion. *Brit. J. Phot.* **24**: 603. 1877 (Dec. 21).

⁷ W. de W. Abney: Theory of the Destruction of the Photographic Image by Time. *Brit. J. Phot.* **24**: 617. 1877 (Dec. 28).

⁸ W. de W. Abney: *Brit. J. Phot.* **24**: 617. 1877 (Dec. 28).

*Although outside the scope of this discussion, inasmuch as the ozone was presumably not applied in solution, the inherent interest of the subject seems to justify the quoting of Abney's continuing words: "Now, if this destruction were caused by an oxidation of the silver atom it should also be oxidized by ozone, since metallic silver when moistened can be oxidized by it. To test this, iodide and bromide films were prepared, exposed under the proper conditions, and, after washing, left to the action of ozone, and in every case where proper precautions were taken the image was entirely destroyed."

Abney⁹ states that he finds that silver iodide wet-collodion plates when uniformly exposed, washed, and then bathed in a dilute solution of either potassium permanganate or potassium dichromate and exposed to the spectrum, show reversal in the red with the greatest facility, and that a silver bromide gelatin plate, uniformly exposed to white light and bathed in dilute potassium dichromate solution, likewise shows reversal in the red of the spectrum.

In the *British Journal of Photography*¹⁰ are described some experiments on the effect of treatment with solutions of potassium dichromate and chromic acid on the latent image on gelatin emulsion plates for development with ferrous oxalate. A five per cent potassium dichromate solution allowed to act for periods from one minute to one hour, followed by thorough washing, entirely fails to remove more than one step of the Warnerke tablet exposure, but greatly diminishes the contrast. The article concludes: "But if bichromate alone be practically insufficient to undo the effect of even faint impressions of light, it is different with solutions containing free chromic acid. A five per cent solution of bichromate to which a few drops of sulfuric acid were added was found after one minute's immersion, to have completely destroyed the image, or, at least, to have put it beyond the reach of the developer, even after several hours' action.

"Now, though in the above experiments bichromate has been shown to fail in destroying the impression of light, it does not follow that it is not useful as a fog-remover, inasmuch as the conditions may be entirely different. If the fog to be removed be but slight, and no subsequent forcing be resorted to in development, it is pretty certain that treatment with bichromate will suffice, as we have proved by bichromating, washing, and re-exposing a plate successfully. But where it is desired to entirely eliminate any previous impression of light free chromic acid must be resorted to."

Writing of general fog as one of the possible defects in gelatin emulsion plates, Abney¹¹ states: "Whatever may be the cause of fog—whether the emulsion itself be at fault, or whether the plates have seen light—we have found that, as in the collodio-bromide process, there is one certain, sure cure. If the emulsion be at fault, squeeze it into water containing 10 grains of potassium bichromate to each ounce and allow it to rest for one hour, and then wash again for a couple of hours

⁹ W. de W. Abney: On the Reversal of the Developed Photographic Image. *Brit. J. Phot.* 28: 391. 1881 (July 29). From *Phil. Mag.* (5) 10: 200-8. 1880 (Sept.).

¹⁰ W. de W. Abney: Potassium Bichromate and the Undeveloped Image. *Brit. J. Phot.* 31: 49. 1884 (Jan. 25).

¹¹ W. de W. Abney: *Photography with Emulsions* 176. Piper and Carter, London. 1885.

more. If all the bichromate be not taken out by this washing, it is not of much consequence, since when dry it is inactive. The sensitiveness, after this treatment, is not much diminished, and the negatives taken with it are beautifully bright. Plates may be treated in precisely the same manner and give unveiled pictures. There is a *slight* diminution of sensitiveness if the bichromate be not all washed out, but nothing to hurt except where very great rapidity is required. Another cure is the addition of a few grains of cupric chloride. This diminishes the sensitiveness slightly, but is most effectual, the negatives yielding bright and brilliant images."

Eder¹² mentions that his observations of the destruction of latent image by potassium dichromate plus sulfuric acid, and by mercuric chloride, were published in the third edition of *Photographie mit Bromsilber-Gelatine* (1886). The *British Journal of Photography* of Jan. 25, 1884, however, acknowledges Abney's prior observation of the destruction of latent image by acidified dichromate.

In an investigation of ammoniacal cuprous chloride as a developer, the Lumière brothers¹³ find that its oxidation product, ammoniacal cupric chloride, is an energetic destroyer of the latent image.

Numerous allusions to the destruction of the latent image on silver halide in collodion or gelatin are given in the second volume of Eder's *Handbuch* (second edition, 1895). It is stated: "If free bromine be added to exposed silver bromide, *etc.*, the latent image is destroyed. Chlorine, iodine, and even oxygen (oxidizing agents) act similarly."¹⁴ Eder states that nitrous acid destroys the latent image, and mentions an observation¹⁵ by Abney of the destruction of a latent image by the nitrous acid liberated in the spontaneous decomposition of the pyroxylin in a silver bromide collodion film. Concerning the action on collodion emulsion, Eder¹⁶ states that "all acids which readily give up chlorine, bromine, or iodine not only prevent fog but are capable of clearing foggy-working emulsions. Tincture of iodine or of bromine, added in small quantity to the collodion emulsion, destroys the fog in the finished emulsion. It works then clearly and more brilliantly, but becomes insensitive after too great an addition of these substances. A bath of aqueous potassium dichromate solution—particularly with the addition of a little hydrochloric acid—

¹² J. M. Eder: *Ausf. Handb. Phot.* III. 882. 1903.

¹³ A. Lumière and L. Lumière: *Propriétés Révélatrices du Chlorure Cuivreux Ammoniacal. Bull. soc. franç. phot.* (2) 3: 294. 1887 (Nov.).

¹⁴ J. M. Eder: *Ausf. Handb. Phot.* II. 32. 1895.

¹⁵ J. M. Eder: *Ausf. Handb. Phot.* II. 87. 1895.

¹⁶ J. M. Eder: *Ausf. Handb. Phot.* II. 385-6. 1895.

destroys the fog on freshly prepared plates or freshly precipitated emulsion." After the addition of a few drops of iodine to clear a collodio-bromide emulsion that has been found foggy in the preliminary test, Eder advises¹⁷ waiting at least twelve hours.

According to Kogelmann,¹⁸ a solarizing exposure on gelatino-bromide plates, bathed in a dilute solution of sodium thiosulfate that has been acidified with sulfuric acid, and washed before development, develops normally as an unreversed negative. The process, however, is said to be uncertain.

Sterry¹⁹ describes experiments on the action of dilute bromine water on gelatin emulsion plates, and finds that "whether applied before or after exposure the effect is always to delay reversal."

R. Namias²⁰ describes the action of an ammonium persulfate solution on the latent image. He notes the entire loss of the latent image of a development emulsion after 5 minutes' immersion in a two per cent ammonium persulfate solution, or a weakening of the image on shorter immersion. No effect on sensitivity is mentioned in this case. In connection with gelatin printing-out paper, he mentions that paper, that had become discolored by keeping, was made white by a few minutes' immersion in an ammoniacal solution of ammonium persulfate. After drying, on printing, a certain loss of strength is observed in the resulting prints; this disadvantage, however, may be entirely obviated by the addition of two per cent of silver nitrate to the persulfate solution.

Englisch²¹ describes an experiment showing the destruction of latent image and enormous reduction in sensitivity caused by bathing a gelatin (Herzog) dry plate in concentrated aqueous bromine. Similar results were obtained by E. Albert with collodion plates. Englisch remarks that there appears to be an especially firm retention of free bromine by the silver bromide grains.

Luther²² observes that while a certain solution of potassium chromate, chromic sulfate, potassium chloride, and hydrochloric acid, having an oxidation potential of about 1.45 volts, is just able in a given time to bleach certain printed-out photometer fields on a pure silver chloride film on glass, another solution of the same substances but with less potassium chlo-

¹⁷ J. M. Eder: *Ausf. Handb. Phot.* II. 401. 1895.

¹⁸ F. Kogelmann: *Eder's Jahrbuch* for 1895. 419.

¹⁹ J. Sterry: *Phot. J.* 38: 270-4. 1898 (April).

²⁰ G. Pizzighelli: *Phot. Korr.* 36: 216. 1899 (April).

²¹ E. Englisch: Über die Einwirkung von Brom auf das latente Bild. *Archiv wiss. Phot.* 1: 282. 1899 (Nov. 1).

²² R. Luther: *Z. physik. Chem.* 30: 654-5. 1899 (Dec. 30).

ride and hydrochloric acid and so having an oxidation potential of about 1.35 volts fails to bleach similar fields under the same conditions. The stronger bleaching solution removes also all the fields not directly visible, but developable in an ordinary developer; while the weaker solution removes only one or two of the latent image fields. For silver bromide on glass, solutions of potassium chromate, chromic sulfate, potassium bromide, and sulfuric acid, are used; and it is observed that while a solution having an oxidation potential of 1.19 can bleach the printed-out fields and remove the whole of the latent image, one having an oxidation potential of 1.09 volts will fail to do so. It seems to follow that an equally high oxidation potential is necessary for the destruction of the latent as for that of the print-out image. The two images are apparently of the same chemical compounds. Luther further remarks that "from the fact that no mere weakening but either complete action or none at all ensues, it is to be concluded that probably the darkened image consists of a mixture of two phases of constant composition and not of a solid solution of variable composition." As the oxidation potential of ferric chloride solution is about 1.0 volt (Peters: 1898), this solution should not be capable of bleaching darkened silver chloride. Wetzlar's and Carey Lea's experience, which, however, Luther is unable to confirm, was to the contrary, and Luther suggests that the positive result recorded may in this case be explained by the action of atmospheric oxygen, the oxidation potential of which is about 1.3 volts. In the reaction with silver, of such solutions as Luther used, a greater or less amount of a chromic chromate²³ is deposited with the silver chloride or bromide. The chromic chromate, owing to its physical condition, may hinder access of the solution to the residual silver relatively much more than does the silver halide. The amount of this deposit increases with decreasing acidity of the chromate solution, and it is possible that its action is negligible in the stronger bleaching solution, but very appreciable in the weaker. From this it would seem that the true oxidation potential for the bleaching of darkened silver chloride and bromide may be somewhat lower than the lower limits found, 1.35 and 1.09 volts, respectively. (For comments regarding action on the *latent* image see Chapter III, p. 87.)

Unaware of the work of Englisch,²¹ Lüppo-Cramer²⁴ investigates the action of bromine water on the sensitivity and latent image of gelatin and collodion emulsions, obtaining results broadly identical with those of Englisch. Using 0.1

²³ E. R. Bullock: *Brit. J. Phot.* **70**: 491-2. 1923 (Aug. 10).

²⁴ Lüppo-Cramer: *Phot. Korr.* **38**: 151. 1901 (March).

per cent bromine in water, and collodion emulsion plates prepared by himself according to von Hübl's directions, Lüppo-Cramer observes, however, a complete destruction of latent image together with, for the same bromine treatment, a reduction in sensitivity to only about one-fourth.²⁴ (Englisch doubtless would have attributed the apparent tenacious retention of bromine to the *gelatin* rather than to the silver bromide itself but for his impression that Albert had found an enormous sensitivity reduction with collodion emulsions, comparable to the effect with gelatin plates. Regarding affinity of bromine for gelatin and collodion, we know at least that a solution of bromine in water or chloroform is freely decolorized by gelatin, while scarcely, if at all, decolorized by collodion or pyroxylin). Lüppo-Cramer records incidentally a fogging action of ammonium persulfate solution, five per cent, on a silver bromide gelatin plate.

The second installment of this article contains several paragraphs so relevant in the present discussion that they are quoted.²⁵

"It is generally known that oxidizing or halidizing agents destroy or at least weaken the latent light-image, and for gelatin plates it is known that these agents depress quite significantly the sensitivity of silver bromide. Because with gelatin plates all these substances may exert an influence in so far as they alter the permeability or other properties of the gelatin, and also in so far as they are not entirely removable from the film by washing, experiments on the effect of these substances on the sensitivity of gelatin dry plates do not give results that can be rigorously differentiated from action on the latent image. With collodion plates this difficulty does not exist, the image support being perfectly indifferent towards many of these agents, and these not being held back in the film to a detectable extent.

"A. Among oxidizing or halidizing agents I tried ferric chloride, cupric chloride, ammonium persulfate, potassium permanganate, potassium ferricyanide, and chromic acid. I employed one per cent solutions of these substances, using as chromic acid a one per cent potassium dichromate solution to which one-twentieth of its volume of 1 : 5 sulfuric acid had been added. I exposed normally in all cases, washed thoroughly, allowed the baths to act for one minute, and again washed thoroughly.

"I. Ferric chloride: The latent image is destroyed; applied before exposure, sensitivity is reduced to between one-sixth and one-eighth.

²⁵ Lüppo-Cramer: *Phot. Korr.* **38**: 218-20. 1901 (April).

"II. Ammonium persulfate (free acid was not added, but a solution that had already stood for twenty-four hours was used): The latent image is not entirely destroyed, the negative appearing to have received about one-tenth of the actual exposure; applied before exposure, sensitivity is only reduced to about one-half.

"III. Potassium permanganate acts strikingly in exactly equal measure before, as after, exposure; in both cases only mere traces of image can be found.

"IV. Potassium dichromate (with sulfuric acid; neutral dichromate generally does not act perceptibly either before or after exposure): The latent image is entirely destroyed, and sensitivity is reduced to about one-fifth.

"V. Cupric chloride	} acts on the latent image appreciably more than before exposure."
"VI. Potassium ferricyanide	

Lüppo-Cramer mentions later that the plates treated with ferric chloride or potassium permanganate were not altered by a subsequent sulfite bath. He finds that the effect of bathing a solarizing sequence of exposures on a collodion plate, for thirty seconds, in one volume of saturated bromine water diluted to one hundred volumes with water, is to remove solarization, a clear negative resulting. On increasing the bromine concentration about sixfold, all trace of print-out image and the whole of the latent image is lost.

Lüppo-Cramer²⁶ mentions that the latent image on collodion emulsion plates is easily destroyed, for post-fixation physical development, by a bath of sodium thiosulfate plus potassium ferricyanide (Farmer's reducer) interposed between fixing and physically developing. He²⁷ exposes a collodion plate in the camera, and after fixing bathes it in saturated bromine water. On physical development no trace of image can be obtained. If, however, plates are exposed for 5 - 10 minutes to direct sunlight after the fixation and bromine treatment, subsequent physical development gives complete, although thin, images. In a further experiment, Lüppo-Cramer gives a full exposure to collodion plates to secure a vigorous image on physical development. Without developing, the plates are fixed, treated with saturated bromine water, washed, and exposed to direct sunlight. After dehydrating in alcohol, dissolving in alcohol-ether, and mixing with unexposed collodion emulsion, a comparison is made with the latter alone as regards behavior on chemical development. For moderate exposures,

²⁶ Lüppo-Cramer: *Phot. Korrr.* 38: 358. 1901 (June).

²⁷ Lüppo-Cramer: *Phot. Korrr.* 38: 559-560. 1901 (Sept.).

to sunlight, of the fixed and bromine-treated film no difference is observed on development in ferrous oxalate. In the case of an exposure lasting ten hours there is a slight differential darkening of the mixture containing the collodion that has thus been exposed, fixed, treated with bromine, and finally intensely exposed.

Namias²⁸ finds that a solution of two grams of potassium permanganate and twenty cubic centimeters of sulfuric acid per liter, completely destroys the latent image on a medium-speed gelatin plate in a few minutes and almost removes sensitivity, the latter being recoverable, however, by means of a bath of dilute ammonia.

R. A. Reiss²⁹ describes the destruction of the latent light-image on silver bromide gelatin plates by mercuric chloride, and the possibility of re-using the plates, after washing, by giving a very full exposure to compensate for their diminished sensitivity.

Lüppo-Cramer³⁰ observes that the latent "chemical fog" of foggy-working gelatin dry plates is not removed by bathing (after exposure and before development) in a one-twentieth saturated bromine water solution for one minute, and washing for one hour in running water, although the latent light-image is partially destroyed, and sensitivity is reduced. This result may be explained by the fact that such a bromine bath as Lüppo-Cramer uses would not in the time allowed penetrate uniformly through the thickness of the gelatin emulsion film but would tend to be retained largely by the gelatin in the upper portion. Chemical fog probably is uniformly distributed; but the effect of a moderate light-exposure, like the action of bromine, is predominantly on the upper portion of the emulsion film. Under the conditions described, therefore, a greater proportionate destruction of the latent light-image as compared with the latent chemical fog may be expected. Lüppo-Cramer observes the absence of latent-fog-destroying action of bromine water when similarly applied to strips of gelatin dry plate that have been bathed for two hours in hydrogen peroxide solutions of concentrations ranging from 0.001 per cent up to 3 per cent and then washed. Such hydrogen peroxide treatment gives, according to increasing concentration, first a feeble action, and then action which increases to a maximum, passes through a neutral zone, and finally diminishes to "glass-clearness." Subsequent bromine treatment, before development, does not alter the result.

²⁸ R. Namias: *Eder's Jahrbuch* for 1901. 169-70.

²⁹ *Eder's Jahrbuch* for 1902. 479.

³⁰ Lüppo-Cramer: Ueber das latente Bild und den sogenannten chemischen Schleier. *Phot. Korr.* 39: 634. 1902 (Nov.).

Lüppo-Cramer³¹ states that Eder has informed him in a written communication that the latent image produced by X-rays on silver bromide in gelatin is destroyed by bromine water or chromic acid.

Lüppo-Cramer³² finds that the edge-fog of stored gelatin emulsion plates is unaffected by bromine water treatment as described in reference 30, but that the pressure fog produced by gently hitting is destroyed. The writer suggests that failure of bromine water to destroy, or diminish, the latent light-image or latent fog, when observed in the experiments described, is due to failure of the bromine to gain access to affected silver halide grains in consequence of retention by the gelatin as it diffuses through the film.

Eder³³ mentions that bromine water (according to Lüppo-Cramer), ammonium persulfate solution (according to Schaum and Braun), and chromic acid solutions, destroy the latent image of a normal exposure and convert the latent image of a solarizing exposure into one that develops normally. He describes experiments with silver bromide gelatin plates and chromic acid (potassium dichromate with sulfuric acid, or potassium dichromate with nitric acid, the latter mixture proving perhaps the more effective). Prolonged action of bromine, according to Lüppo-Cramer, destroys also the latent image of the solarizing exposure.

The consideration of the spatial distribution of the latent image with respect to the volume of the silver halide grain enters into the theory of solarization. With solarizing and greater exposures there is probably a formation of latent image not merely on, but distinctly within, the silver halide grain. In Eder's experiments, and in those to which he alludes, we may consider that in the reversal range of exposures, there is latent image in the *interior* of the silver halide grains. The silver-oxidizing agents named are such as can penetrate but slowly into the silver halide grains, whereas an ordinary chemical developer, owing to its sulfite content, has a comparatively rapid solvent action, so that a considerable portion of the interior image, protected from the oxidizing bath, becomes effective on (somewhat protracted) development.

F. Heyer's inaugural dissertation (Leipsic, 1902), in which he describes his investigations at the instance of R. Luther on the hypothetical silver subchloride, is not accessible to the writer at this time. From later references it seems that Heyer's

³¹ Lüppo-Cramer: *Phot. Korr.* 39: 640. 1902 (Nov.).

³² Lüppo-Cramer: *Phot. Korr.* 39: 639-40. 1902 (Nov.).

³³ J. M. Eder: Herabdrückung der Solarisationsgrenze bei überexponierten Trockenplatten durch Behandlung mit Chromsäure vor dem Entwickeln. *Phot. Korr.* 39: 647. 1902 (Nov.).

experiments have no direct bearing on the latent image (as distinguished from the silver photochloride). Eder³⁴ states that Heyer concludes from electrochemical measurements that the free energy of the reaction $\text{Ag} + \text{AgCl} = \text{Ag}_2\text{Cl}$ does not differ appreciably from zero, and that, contrary to all earlier assertions, there is no ground for accepting the existence of silver subchlorides. Weiss³⁵ and Reinders³⁶ state that Heyer, repeating the earlier potential measurements for silver photochloride but using solutions showing a more constant potential, finds that a ferrous-ferric acetate solution with $N/100$ sodium chloride, and of oxidation potential 0.66 volt, oxidizes pure precipitated silver to a material having the empirical composition $\text{AgCl}_{0.73}$, that is, more than half-way to AgCl , while a similar solution of a somewhat lower oxidation potential (0.62 volt) reduces pure silver chloride to a material of the empirical composition $\text{AgCl}_{0.26}$, that is, more than half-way to Ag . Possibly contrary to expectation, he obtains in this way no evidence in support of the existence of silver hemichloride, Ag_2Cl .

Lüppo-Cramer³⁷ mentions that in the previous year he had observed that in the case of many plate emulsions the latent chemical fog was not destroyed by the action of bromine water but was even increased. He now establishes the fact that all high-speed plates with a certain amount of latent chemical fog actually increase in latent fog on treatment with dilute bromine water. The plates are bathed in one-tenth saturated bromine water for one minute, and then thoroughly washed. As compared with non-bromine-treated plates, the bromine-treated high-speed plates show a perceptible increase in fog on five minutes' development in metol-soda. On the other hand, bromide lantern plates show a destruction of fog.

Vidal³⁸ states that the latent fog on old plates "which have become fogged owing to the time that has elapsed since the date of their manufacture" may be removed by interposing a bath of one per cent potassium dichromate for 3-5 minutes, followed by washing in running water for several minutes between exposure and development, while the latent image, or any fogging due to the action of light, is unaffected by this treatment. Compare reference 10.

Using bleach solutions similar to those of Luther,²² Baur³⁹

³⁴ J. M. Eder: *Jahrbuch* for 1904, 333-4.

³⁵ H. Weiss: *Z. physik. Chem.* **54**: 316-7. 1906 (Jan. 29).

³⁶ W. Reinders: *Z. physik. Chem.* **77**: 359. 1911 (Aug. 1).

³⁷ Lüppo-Cramer: *Phot. Korr.* **40**: 227-8. 1903 (April).

³⁸ L. Vidal: On the Utilization of Old Sensitized Plates which have become Fogged. *Phot. J.* **43**: 220. 1903 (Aug.).

³⁹ E. Baur: *Z. physik. Chem.* **45**: 617-21. 1903 (Nov. 24).

makes experiments to determine the potential required for oxidation (more exactly, chloridation) or reduction of synthetic silver photohalide preparations of composition ranging from 55 to 99 molecular per cent silver chloride. The attainment of equilibrium is hastened by the use of a steam-oven. Solutions of oxidation potential 1.37 and 1.33 volts bleach silver photochloride of every composition. The solution of oxidation potential 1.25 volts is observed to change the color of silver photochloride of both higher and lower chlorine content to that of 88.1 - 89.2 molecular per cent silver chloride, so that, judging the composition from the color, there is an attainment of equilibrium from either side. Baur, however, is not convinced that such judgment is correct. Chemical analysis of the solid reaction products, after washing, would remove the uncertainty.

Eder⁴⁰ states that the latent image on silver bromide in gelatin emulsion is destroyed by tincture of bromine, tincture of iodine, ferric chloride, cupric chloride, mercuric chloride, auric chloride, nitrous acid, potassium dichromate, potassium ferricyanide, and ferric oxalate. (The list actually given is a more lengthy one, but, as in some other instances, there are cited from the original reference such substances only as are classed as silver-oxidizers in this discussion.)

Eder⁴¹ mentions as substances that destroy latent chemical or light-produced fog in gelatino-bromide emulsions,—tincture of iodine, bromine, chlorine, potassium dichromate, dichromate with hydrochloric acid, dichromate with nitric acid, and dichromate with sulfuric acid.

Homolka⁴² describes the development by means of a solution of gold chloride, of latent images on high-speed gelatin plates, bromide paper, and gelatin and collodion printing-out papers. His account of the method for plates, is as follows: "The plates (Lumière Blue Label) were exposed briefly—about 1/50 sec.—, in fine weather, and placed in the developing bath (0.1 per cent gold chloride in distilled water) in the dark, and left for about 10 - 15 hours; then fixed in the ordinary acid fixing bath. The image appears blue by reflected light, and copper-red and thin as breath (*hauchartig dünn*), but with the most delicate details, by transmitted light. If a longer exposure be given, the image does not appear clear, while the entire plate is covered by a copper-red veil." For pure whites on bromide papers, it is necessary to acidify the

⁴⁰ J. M. Eder: *Ausf. Handb. Phot.* III. 72. 1903.

⁴¹ J. M. Eder: *Ausf. Handb. Phot.* III. 90. 1903.

⁴² B. Homolka: Ueber die Entwicklung des latenten photographischen Bildes mittelst Chlorgold. *Eder's Jahrbuch* for 1903. 104.

developer slightly, as by the addition of 0.4 - 0.5 gram of syrupy phosphoric acid to a liter of the gold chloride solution. Printing-out papers are briefly exposed (as for development with a usual acid hydroquinone or pyro p.-o.-p. developer), washed in distilled water, and placed in the developing bath of gold chloride and phosphoric acid for 2 - 3 hours, rinsed, and fixed in the acid fixing bath. The image is of a beautiful blue-violet color, and vigorous, yet reproducing the most delicate details. Gold chloride and silver react to form gold and silver chloride. Assuming that the latent image consists of silver (element), this is replaced on immersion in the gold chloride bath by a latent image consisting of gold (element). Gold chloride solution in contact with gelatin or paper is slowly reduced even at room temperature to the element, giving a very dilute colloidal gold solution which acts slowly as a physical developer or intensifier of the invisible or, as in the case of the printing-out emulsions, barely visible, image of gold.

In the chapter on the effect of additions of foreign substances to gelatino-bromide emulsion in his *Ausführliches Handbuch der Photographie*, Eder⁴³ mentions the following substances as tending to destroy or destroying latent chemical or light-produced fog: bromine, chlorine, mixtures liberating chlorine, ferric chloride, cupric chloride, other "metal perchlorides," potassium dichromate, potassium dichromate plus mineral acids, potassium chlorate with hydrochloric acid, chloric acid, and potassium ferricyanide. Sensitivity is lowered by bromine, iodine, chlorine, the metal perchlorides, ferric oxalate, potassium dichromate, potassium dichromate with mineral acids, chloric acid, and potassium ferricyanide.

According to Lüppo-Cramer, Reiss⁴⁴ found that chlorine has a fogging action on dry plates.

Sterry⁴⁵ finds that a ten per cent potassium dichromate solution fails in five hours to destroy any of the most minute detail of a latent image on a gelatin emulsion plate. The density curve is so modified, however, that great contrasts are correctly rendered. He says: "Papers of the Velox and Gravura type require very thin negatives; but the application of one part in 1000 of potassium dichromate for one or two minutes between exposure and development, will so alter the gradation that a good print may be obtained from a negative specially developed for carbon printing. Very slow lantern plates in the same way will give soft positives from strong negatives." This

⁴³ J. M. Eder: *Ausf. Handb. Phot.* III. 132. 1903.

⁴⁴ R. A. Reiss: See *Photographische Probleme* 133. 1907.

⁴⁵ J. Sterry: The Separation of Development into Primary and Secondary Actions. Consequent Effect upon the Correct Rendering of Light Values and Theory of the Latent Image. *Phot. J.* 44: 50. 1904 (Feb.).

action of dichromate is sometimes referred to as the "Sterry effect," but was described essentially, twenty years earlier, in the *British Journal of Photography*, the editor being W. B. Bolton.

Waterhouse⁴⁶ states that he found that even a saturated solution (about ten per cent) of potassium dichromate does not readily destroy the latent image, but that a "very weak solution of the bichromate with nitric acid, about one per cent of each, did so."

In an article on the relation between grain-size and solarization, Lüppo-Cramer⁴⁷ shows photomicrographs illustrating the action of an intervening bath of Eder's solution of potassium dichromate with nitric acid,³³ followed by washing, in allowing normal development (*i.e.*, to a direct density sequence) of a solarizing exposure.

Eder mentions that chromic acid, mercuric nitrate, or potassium ferricyanide, destroys the developability of a wet collodion plate. He states⁴⁸ that the latent image on silver chloride collodion plates is destroyed by *aqua regia*, perchlorides, potassium ferricyanide, or mercuric nitrate.

Sheppard and Mees⁴⁹ describe experiments on the action of chromic acid solution on gelatin emulsion plates (Wratten Ordinary). After rotation in chromic acid solution, and then in water, development gives a density curve which is distorted at the top, inertia and gamma-infinity being unchanged. The velocity of development is diminished, approximately in proportion to the logarithm of the concentration of the chromic acid solution if the logarithm of 0.01 per cent is taken as unity. They conclude that this effect, which is diminished either by diminishing the time of immersion in the chromic acid solution or by prolonging the subsequent washing, is due to an irreversible adsorption of chromic acid in the film. On treating the chromated plates with sodium sulfite solution, the velocity constant of development reassumes its normal value. It is then seen that with increasing times of treatment in the chromic acid, gamma diminishes and the inertia increases. This enables the authors "to decide without doubt that the prolonged action of chromic acid destroys the latent image." "The rate of attack on the latent image was found to increase very rapidly with the concentration of the CrO_3 ."

Sheppard and Mees⁵⁰ mention a diminution in sensitivity by the action of solutions of simple salts of bivalent copper,

⁴⁶ J. Waterhouse: *Phot. J.* **44**: 57. 1904 (Feb.).

⁴⁷ Lüppo-Cramer: *Phot. Korr.* **42**: 257-9. 1905 (June).

⁴⁸ J. M. Eder: *Ausf. Handb. Phot.* I. 2. 276. 1906.

⁴⁹ S. E. Sheppard and C. E. K. Mees: The Action of Substances upon the Latent Image. *Phot. J.* **47**: 65. 1907 (Feb.).

⁵⁰ S. E. Sheppard and C. E. K. Mees: *Proc. Roy. Soc.* **A78**: 464. 1907 (Feb. 2).

bivalent mercury, and trivalent iron, and a destruction of latent image by copper sulfate solution, the treatment with the metal salt solution being followed in all cases by prolonged washing. In the writer's opinion, the effects observed in the case of copper sulfate and possibly other non-halogen metal salts were probably due largely to the joint action of the traces of soluble chlorides or bromides unintentionally present.

Sheppard and Mees⁵¹ state that "oxidizing ferric-ferrous oxalate solutions which bleached negatives and would not develop had no destructive effect on the latent image, the potential of which is, therefore, considerably different from metallic silver."

Sheppard and Mees⁵² confirm the observation of Homolka⁴² of the development of a latent image with gold chloride solution. A plate is exposed and then treated for twelve hours with *M*/100 auric chloride solution. An image of metallic gold, yellow by transmitted, and red by reflected, light, is formed. Density measurements give a $\log i$ of 2.1 (comparing with 1.96 for ordinary development), and a γ_{∞} of 0.021. The authors say: "This action might possibly be due to a form of so-called physical development. We have already seen that gelatin reduces gold to the metallic state, and this would then, just like silver from a supersaturated solution, be deposited on the latent image." An attempt to repeat the experiment with gelatin-free silver bromide gives uncertain results, but traces of a visible image are formed on the highest exposures, so that apparently the latent image can bring about the chemical change— $\text{Au}^{+++} \rightarrow \text{Au}$. They suggest that possibly "more definite information as to the potential of the latent image may be obtained by further experiments on these lines with gold chloride."

Sterry⁵³ finds that a latent image on "gaslight paper" may be bathed in a saturated solution of potassium dichromate for twelve hours, washed, cleared in potassium metabisulfite, and then developed without any loss, although the image may develop more slowly. From other experiments he concludes that "by means of potassium dichromate, chromic acid, potassium permanganate, bromine, *etc.*, there is a changed condition brought about in part of the *light reduction* product, which apparently may greatly delay or prevent development of this

⁵¹ S. E. Sheppard and C. E. K. Mees: *Investigations on the Theory of the Photographic Process*. 111. 1907. Longmans, Green and Co., London.

⁵² S. E. Sheppard and C. E. K. Mees: *Other Chemical Actions of the Latent Image. Investigations on the Theory of the Photographic Process*. 266. 1907. Longmans, Green and Co., London.

⁵³ J. Sterry: The Action of Oxidizers upon the Development of the Latent Image. *Phot. J.* 47: 170. 1907 (March).

portion entirely." Sterry considers that there are some indications that light produces two distinct developable images, namely, "a product which is untouched by oxidizing agents and probably is removed by the fixing bath," and "that product which is prevented from being developed by oxidizing agents and is apparently removed after oxidation by the fixing bath." As explained in Chapter II, it is possible that such differences may be largely the result of differences, with increasing exposure, in the grain-spatial distribution of the latent image.

Demole⁵⁴ describes some effects of potassium ferricyanide on the latent image of "a photographic plate." "On immersing an exposed plate for a few minutes in a one per cent solution of potassium ferricyanide, and then rinsing and developing in hydroquinone, two remarkable facts are observed: first, the plate may have received a heavy overexposure without development being accelerated in consequence, and without the result being affected in the least ('ni que le résultat en soit le moins du monde compromis')—the oxidant plays the rôle of regulator of time of exposure—; second, if development be carried out by the white light of a candle the image obtained will be a positive instead of a negative as it would have been if development had taken place by red light." It is not entirely clear whether Demole means that potassium ferricyanide is a corrective of solarization in its action on the latent image. The second effect mentioned is of interest. In the Albert reversal experiment,⁵⁵ as described for collodion plates, the sequence of operations is as follows:—giving a step exposure, bathing in nitric acid, exposing uniformly, developing. J. Precht⁵⁶ "refined" the experiment by substituting an exposure to a picture, as in the camera or behind a positive or negative, for the step exposure. The general Albert-Precht effect, as it may be called, is possibly identical, fundamentally, with the second effect now described by Demole. The manner of impressing the second, uniform exposure is important. Actinic light falling on an emulsion film during development, in consequence of the partially developed image in the upper portion of the film acting as a negative in contact with less-exposed emulsion beneath, may give rise to an uncertain or reversed result, a new positive being formed which tends to predominate on prolonging the development. The procedure in the Demole experiment must, therefore, be so modified that the whole of the

⁵⁴ E. Demole: Contribution à l'étude de l'image latente photographique. *Comp. rend.* **144**: 565. 1907 (March 11).

⁵⁵ E. Albert: *Archiv wiss. Phot.* **1**: 285. 1899 (Nov.).

⁵⁶ E. Englisch: *Archiv wiss. Phot.* **2**: 233-4. 1900 (Nov.).

second exposure is made prior to development, which is carried out by a safe light. Under these conditions, according to tests made with Eastman Speedway plates and Super-Speed Portrait film, in April, 1925, little or no trace of reversal can be observed, and the effect cannot be regarded as established.

A. and L. Lumière and A. Seyewetz⁵⁷ describe a reversal process, in one operation of which there is a dissolution of the silver of a developed image, by a bath of acid permanganate, and simultaneous survival of a latent image which on subsequent development gives the required reversal image. Practical success being dependent on the processing conditions, these are quoted in detail. The plates are exposed normally, developed fully in an ordinary developer such as diamino-phenol, and rinsed for about a minute. Unless backed or non-halation plates are used, the plates are placed against a black ground, such as a sheet of black paper, which is made to adhere by moistening, so that the light in the subsequent exposure may act only from above. The plates are exposed heavily to any convenient source, for example, to a No. 2 Welsbach burner for ten to fifteen minutes at 20 inches, or to 24 - 28 inches of burning magnesium ribbon of about one-eighth inch width at a distance of about 8 inches. The acid permanganate bath, then used to dissolve the developed silver without removing the latent image, is as follows:—Potassium permanganate, 1 gram; concentrated sulfuric acid, 10 c.c.; water, 1 liter. Of this, about 200 c.c. may be used for a 5 by 7 inch plate, the plate being immersed in the darkroom until the image is completely removed. The plates are then treated with a weak bath of sodium bisulfite, and rinsed briefly, then fixed in 10 per cent hypo solution, and washed thoroughly. The physical developer for the second development is:—*A.* Anhydrous sodium sulfite, 180 grams; mercuric bromide, 9 grams; water, 1 liter. *B.* Anhydrous sodium sulfite, 20 grams; metol, 20 grams; water, 1 liter. For use on a 5 by 7 plate, 150 c.c. of *A* are mixed with 40 c.c. solution *B*. "The image appears after about a minute, but gains strength slowly. By continuing the action of the developer for a sufficient time, from one hour to an hour and a half, the image is obtained in finest detail with the dense portions as vigorous as those of a negative developed by the customary alkaline method.

"Although the time of the re-development is considerable, the solution remains perfectly usable throughout. It should be noted that an acid solution of potassium dichromate, which frequently is preferably employed in development after fixing,

⁵⁷ A. Lumière, L. Lumière, and A. Seyewetz: *Reversed Negatives Direct by Development after Fixing*. *Brit. J. Phot.* 58: 851. 1911; from *Agendu Lumière* 215. 1907.

cannot be used in this method since it partially destroys the latent image which is left after fixing." In comment it must be remarked that the second, flash, exposure prescribed being greatly in excess of any normal exposure for a medium- or high-speed gelatin emulsion, the latent image produced will be largely in the interior of the silver halide grains. The more deeply seated portions are unaffected by the relatively brief permanganate treatment required for the dissolution of the developed silver grains, yet are available, in so far as they are not removed by the joint action of the hypo and atmospheric oxygen, as nuclei for post-fixation physical development. The authors state that acid dichromate cannot be used since it partially destroys the latent image, but the present writer would point out that acid permanganate likewise partially destroys the latent image, and hypo in contact with air again partially destroys the remainder, so that the process is in no sense quantitative, but the result is dependent upon the experimental conditions. Assuming sufficiency of volume and time of action of the acid permanganate bath, it is difficult to understand the smaller loss of latent image in this process than when acid dichromate is used, since the former bath has by far the faster action on the latent image of a non-solarizing exposure when solutions of the same (moderate) normality with respect to oxidation-reduction reactions and with the same normality of added sulfuric or nitric acid are used. It may be suggested, that with the low concentration of potassium permanganate in the bath recommended as compared with usual concentrations of dichromate, there is, in the case of the permanganate and not in the case of the dichromate bath, an approach to exhaustion of the oxidizing substance during the reaction.

The Albert experiment ("Albert-Versuch" of the German literature)⁵⁵ is not within the scope of this discussion since the silver solvent employed is nitric acid, which, owing to the extreme slowness of its initial reaction when in dilute solution, is not considered as a silver-oxidizer in this volume.

Lüppo-Cramer⁵⁸ mentions, however, a variation of the experiment in which chromic acid or ammonium persulfate, 2.5 per cent solution, for fifteen hours, is used instead of nitric acid, and high-speed gelatin instead of collodion plates. In this variation, there is given a strongly solarizing first exposure. (The first exposure in the Albert and Precht experiments was presumably not quite as great as this, since Lüppo-Cramer merely states that it was very full, *sehr reichlich*, but the information is scanty, and it does not seem possible to arrive at a definite

⁵⁸ Lüppo-Cramer: *Phot. Korrr.* 46: 495. 1909 (Oct.).

opinion.) Giving a solarizing first exposure and treatment with chromic acid or persulfate as mentioned above, thorough washing, and then a brief uniform exposure, Lüppo-Cramer observes reversal on either chemical or physical development.

Lüppo-Cramer⁵⁹ mentions that, like bromine water (ref. 37), potassium ferricyanide, potassium permanganate, ferric chloride and cupric chloride act faster on the latent image of gelatin plates than on the chemical fog, and further, that all these substances in certain concentrations, increase slightly the normal fog of ripened emulsions. Persulfate fogs a high-speed gelatin plate intensely under conditions of partial destruction of a light-image.

Perley, from experiments in which Seed or Cramer Lantern plates were bathed in a solution of hypobromous acid or potassium permanganate, then exposed and developed in a carbonate-hydroquinone developer,⁶⁰ concludes that "oxidizing agents do not increase the tendency towards solarization," and that "a chemical which dissolves silver from the latent image will check solarization."⁶¹

Perley appears to have misread the description of Abney's experiments to which he refers. Abney obtained reversal of a first, white-light exposure made in absence of the oxidizing agent, by a second, red-light, exposure in its presence, while Perley looks for and fails to find an acceleration of reversal by the presence of the oxidizing agent when a single intense, white-light exposure is given.

Lüppo-Cramer⁶² finds that collodion emulsion plates, prepared without any addition of chemically reducing substances, and in which, therefore, the absence of silver germs may be assumed, are unaffected in sensitivity by treatment with chromic acid solution. He contrasts their behavior with that of ripened gelatin emulsion plates, whose sensitivity is reduced by chromic acid treatment.

Wilsey⁶³ finds that measurements on different development papers confirm the result obtained by Sterry, that immersion in dilute potassium dichromate solution after printing and before development, gives a great reduction of contrast and increase of scale, with little loss of maximum black and that there is no loss of quality or speed.

⁵⁹ Lüppo-Cramer: *Photographische Probleme* 132. 1907.

⁶⁰ G. A. Perley: *J. Phys. Chem.* **13**: 630-5. 1909 (Nov.).

⁶¹ G. A. Perley: *J. Phys. Chem.* **14**: 707-8. 1910 (Nov.).

⁶² Lüppo-Cramer: *Koll.-Zeits.* **16**: 160. 1915 (May-June).

⁶³ R. B. Wilsey: The Reduction of Contrast and Increase of Scale of Photographic Papers. *Kodak Abstract Bulletin* **3**: 194. 1917 (Nov.).

Kropf⁶⁴ finds, in agreement with Lüppo-Cramer's experience as stated in *Photographische Probleme*⁶⁵ (and previously³⁷), that the addition of bromine to foggy emulsions is seldom favorable, in most cases no effect being observed, and sometimes an actual increase in fog being produced.

Renwick⁶⁶ states that "E. Albert found that if, after giving an exposure to a plate coated with a collodion emulsion, it is treated with a silver solvent (e.g., nitric or chromic acid), then washed and re-exposed to diffused light, a reversed (positive) picture is obtained on development." Albert⁵⁵ does not appear to have used, or mentioned the use of chromic acid: this modification is apparently due to Lüppo-Cramer.⁵⁸ As published in the *British Journal of Photography*⁶⁷ the wording is "a silver solvent (e.g., chromic acid)." Thus "nitric acid" has become "chromic acid"! In a case such as this, in which the effect under discussion still awaits a satisfactory explanation, great care is excusable in attempting to preserve the correctness of an original description.

According to German patent 346851, of Oct. 26, 1920,⁶⁸ issued to Farbenfabriken *vormals* Friedrich Bayer und Co., for a process for decreasing the sensitivity of photographic silver halide emulsions, sulfur, in the form of flowers, an emulsion, or a solution, is added to the finished emulsion, which is then stirred for half an hour, the sensitivity being reduced, without increase in the tendency to fog. A gaslight emulsion thus treated gives brown tones on development. Considerable quantities of sulfur or of allied elements may be used.

According to German patent 351905, of March 8, 1921⁶⁹ also issued to Farbenfabriken *vormals* Friedrich Bayer und Co., for brown-tone printing-out emulsions, brown tones are obtained by adding an element of the sulfur group to the prepared emulsion and fixing in an ordinary acid fixing bath. A solution of sulfur in carbon tetrachloride is added in the case of collodion emulsions, and to gelatin p.-o.-p. emulsions a solution of sulfur in carbon tetrachloride with an oil is added. Selenium and tellurium have the same action.

Steigmann⁷⁰ asserts that inasmuch as silver mercurous chloride (HgAgCl_2), produced by the interaction of mercuric chloride and silver, is very easily reducible as compared with

⁶⁴ F. Kropf: *Phot. Korr.* **56**: 142. 1919 (May).

⁶⁵ Lüppo-Cramer: *Photographische Probleme* 132. 1907.

⁶⁶ F. F. Renwick: *J. Soc. Chem. Ind.* **39**: 162T. 1920 (June 30).

⁶⁷ F. F. Renwick: *Brit. J. Phot.* **67**: 467. 1920 (July 30).

⁶⁸ *J. Soc. Chem. Ind.* **41**: 310A. 1922 (Apr. 29).

⁶⁹ *J. Soc. Chem. Ind.* **41**: 729A. 1922 (Sept. 30).

⁷⁰ A. Steigmann: Ueber den Einfluss von Sublimat auf das latente Bild. *Phot. Ind.* **19**: 296. 1921 (April 13).

silver chloride (AgCl) produced by the action of cupric chloride on silver, it might be expected, from the silver germ theory of development, that mercuric chloride would act as an intensifier of the latent image. The resulting silver mercurous chloride being immediately reduced by the developer to silver together with an equivalent of mercurous mercury, the number of germs should be doubled. Actually, however, a mercuric chloride solution progressively weakens and eventually destroys a latent image, for chemical development, as also does a solution of a double mercuric thiocyanate (Agfa intensifier). Steigmann attributes this to a "poisoning" of the silver germs by mercury. He considers that if mercuric chloride solution is not a destroyer of the latent image for post-fixation physical development with mercury, that fact would be a strong support to the silver germ adsorption theory.

Jordan and Burns,⁷¹ in a note on desensitizing plates for stellar parallax work, state: "To secure a greater range of magnitude reduction than is attainable with the ordinary rotating sector, the Allegheny Observatory is now desensitizing a central area of the photographic plate before exposure. The method consists of the application of a one per cent solution of copper sulfate for 5 minutes. This is then wiped off and the plate dried with a fan, at a temperature of 64 - 70° F. The sensitiveness is reduced about fifty times; the grain of the plate remains unchanged, and tests indicate no reduction in accuracy."

Sheppard⁷² has found that the desensitizing action of chromic acid is not confined to the fastest, largest-grained negative emulsions, but extends to all emulsions, including the almost insensitive, grainless Lippmann emulsion and positive chloride emulsions.

For the utilization of undeveloped fogged plates, Chierchia⁷³ prescribes immersion in a solution of 20 grams of potassium dichromate and 3 c.c. of nitric acid in 1 liter of water, washing, and drying in the dark. The speed may be somewhat reduced. Developed, but not fixed, plates, after washing out all traces of developer, are bathed in a solution of 50 grams of potassium bromide, 30 grams of potassium dichromate and 30 drops of sulfuric acid, in 1 liter of water. When bleached, they are washed thoroughly, treated for a few minutes with 5 per cent ammonia, washed for 30 minutes, and dried.

Steigmann⁷⁴ finds that mercuric chloride greatly weakens the latent image on Perutz Lantern plates for post-fixation

⁷¹ F. C. Jordan and K. Burns: On Desensitizing Plates in Parallax Work. *Popular Astronomy* 29: 629. 1921 (Dec.).

⁷² S. E. Sheppard: Die Silberkeimtheorie der Entwicklung. *Phot. Korr.* 59: 76. 1922.

⁷³ G. Chierchia: Utilization of Fogged Plates. *Corr. Fot.* 19: 3982. 1922 (May).

⁷⁴ A. Steigmann: Untersuchungen am latenten Bild. *Phot. Ind.* 20: 448. 1922 (May 17).

physical development in either a (Lumière-Seyewetz) mercury or silver developer. This fact, and the non-destruction by a solution of potassium ferricyanide and potassium bromide, of the latent image for chemical development, appear inconsistent with either the silver germ or the silver subhalide theory. A solution of potassium ferricyanide and sodium thiosulfate or of mercuric nitrate completely destroys the fixed latent image for physical development. The difference in the behavior of ferricyanide plus bromide on the one hand, and of mercuric nitrate or ferricyanide plus thiosulfate on the other, affords, Steigmann considers, proof of the correctness of the silver germ, or alternatively, the silver subhalide theory of the latent image. In the one case the latent image substance is converted to silver bromide, which, on becoming reduced, affords fresh latent image, corresponding to a weakening of the latent image; and in the other, it is dissolved by the bath, corresponding to a destruction of the latent image. Steigmann remarks that "still more convincingly than by the foregoing experiments the presence of metallic silver in the fixed latent image is supported by the fact that by bathing in hypo *after the treatment* with potassium ferricyanide plus potassium bromide the latent image is completely destroyed. This destruction is only possible if silver bromide is produced from the exposure germ of metallic silver by the action of the bath of ferricyanide plus bromide, and then dissolves readily in the subsequent thiosulfate bath." The action of a solution of ferricyanide alone on a latent image for chemical development is slower than that of a solution of ferricyanide plus bromide. A fully exposed plate may be bathed in mercuric chloride solution and developed by the white light of a 50 candle-power metal-filament lamp without fogging, or at least without fogging as quickly as if it had been bathed instead in a solution of cupric chloride, ferricyanide plus bromide, or quinone plus bromide, but, owing to progressive destruction of latent image, mercuric chloride, unlike phenosafranine, can be used as a desensitizer only in case of heavy overexposure. When added to the chemical developer, mercuric chloride, probably because of formation of the complex salt, sodium mercuric sulfite, becomes inactive, affecting neither sensitivity nor latent image. Steigmann is apparently unaware of Lüppo-Cramer's work²⁷ in 1901 on the apparent destruction of the latent image after fixing, by bromine water, and its subsequent re-creation by exposure to light, or he would, after fixing and then treating the latent image with halidizing agents, consider exposure or non-exposure to actinic light before or during the treatment with the physical developer. An observed apparent complete destruc-

tion of latent image for silver physical development by the operations of bathing in ferricyanide plus bromide, washing, fixing in hypo, and again washing, is of doubtful significance unless exceptional care has been taken in the experimental conditions. Inadequacy of first washing, or the presence of free sulfur in the fixing bath, for instance, may lead to loss of latent image.

Lüppo-Cramer⁷⁵ mentions a fogging action of ferric and cupric salts. On bathing dry plates in freshly prepared 0.1 - 0.5 per cent—not more concentrated—solutions of ferric chloride, ferric ammonium citrate, potassium ferric oxalate, or cupric sulfate, and drying, fog is found on development in metol-hydroquinone. This fog, which is independent of the diminution in sensitivity, Lüppo-Cramer attributes to the same cause as that produced by basic dyes—the colloidal ferric or cupric hydroxide, as formed by hydrolysis and retained in the gelatin, acting in the same manner as the dye base. Fog due to the action of ferric or cupric salts may be prevented by the use of phenosafranine either as a bath before development or as an addition to the developer.

Lüppo-Cramer⁷⁶ finds that prior treatment with chromic acid prevents this fogging effect.⁷⁵ He finds a similar preventive action for the fog produced by a basic dye, as illustrated by the following experiment:—Plates are bathed in a one per cent potassium iodide solution for two minutes, and after washing treated with chromic acid mixture, followed by a bath of ten per cent potassium nitrate solution to secure the complete removal of the chromic acid. These plates, and plates treated with the potassium iodide only, are bathed in a 0.005 per cent Janus Green *B* solution, and developed, the latter remaining clear while the former fog completely. Removal of ripening-reduction germs (Reifungsreduktionskeime), by the potassium iodide and chromic acid treatment, thus prevents entirely the fogging action of either metal salts or basic dyes.

Clark^{77, 78} describes experiments on the effect of chromic acid on sensitivity, with especial reference to the accelerating effect of a preliminary light-exposure on the lowering of sensitivity by chromic acid solution. He shows that by treatment of a fast plate with chromic acid after a preliminary exposure "sufficient in each case to render developable practically 100

⁷⁵ Lüppo-Cramer: Ueber die Verschleierung der Bromsilberplatte durch Metallsalze. *Phot. Ind.* 20: 726. 1922 (Aug. 16).

⁷⁶ Lüppo-Cramer: Zur photographischen Wirkung von Metallsalzen und Farbstoffen. *Phot. Ind.* 20: 900. 1922 (Oct. 18).

⁷⁷ W. Clark: *Phot. J.* 63: 233-5. 1923 (May).

⁷⁸ W. Clark: *Trans. Faraday Soc.* 19: 309-11. 1923 (Nov.).

per cent grains of the untreated plate," the speed can be reduced to a minimum of 5 H. and D. It is also pointed out that by this exposure to light before treatment with chromic acid the time of desensitization is much reduced. Only once does Clark give complete information regarding the preliminary exposures. This is in connection with an illustration giving comparative cross-wedge diagrams of a commercial ultra-rapid plate, before and after preliminary exposure and chromic acid treatment. This preliminary exposure is for 15 seconds at 6 feet from a 100 c.-p. lamp (corresponding, for high-speed emulsions, to the "overexposure" portion of the density curve, and being distinctly less than that required to produce a barely perceptible print-out image).

Sheppard, Trivelli, and Wightman⁷⁹ investigate the desensitizing action of chromic acid solution on single-grain layers of a diluted high-speed emulsion (Seed Graflex).^{*} These experiments on desensitizing with chromic acid solution indicate that nuclei are present before exposure and that the alteration of the sensitivity by the desensitizing agent is a function of the grain-size. They state that recent experiments have indicated that the nucleus area increases with grain-size and that this may be connected with the great resistance of the larger grains to desensitizing agents. The facts may be summarized as follows:—(1) Chromic acid desensitizes in the "toe" of the curve more than in other parts. (2) Chromic acid applied *after great exposure* removes reversal. (3) Chromic acid *present* in exposure holds up latent image formation. The chromic acid was removed by washing in a feebly alkaline (potassium bicarbonate) solution, and then in distilled water; development was in pyro-carbonate.

⁷⁹ S. E. Sheppard, A. P. H. Trivelli, and E. P. Wightman: *Trans. Faraday Soc.* **19**: 306-8. 1923 (Nov.).

^{*}The method of preparing the single-grain-layer plates is as follows:—"The sensitive emulsion on the original plate or film is soaked for 30 minutes in distilled water preferably at 15° C. and not over 20° C. This expands and softens the gelatin but does not remove any of it. The water is then poured off and 45 c.c. of 1 per cent solution of gelatin in 15 per cent ethyl alcohol-water at 40° are added. The whole is then placed in an oven at 40° for 10 minutes, taken out from time to time to rock the tray and thus remove the melted gelatin. After pouring the mixture into a volumetric flask, covered with asphaltum paint, 25 c.c. more of the gelatin solution in alcohol water are added, and the tray is again placed in the oven for about 2 minutes. The second lot is poured into the flask and the process is repeated a third time with 25 c.c. of the gelatin solution. With some kinds of emulsions it is necessary to use a larger volume, 250 c.c. or even 500 c.c., because of the excessively large number of particles contained in a unit quantity of it. The size of plate ordinarily employed is 7 x 5 inches (17.8 x 12.7 cm.). A number of 5 x 2 inch strips, cut from larger plates that had been 'subbed' with a thin coating of hard gelatin, were placed on the glass platform of the chill-box and 1 c.c. of the emulsion suspension was spread evenly on each strip. The strips were immediately slid on to the level metal plate which was then slid into the cooling chamber. Here they remained for 30 minutes, by which time the gelatin was set sufficiently so that it would dry completely without remelting. The drying was completed on level shelves in a light-tight drying cabinet, in which the temperature was kept below 20° C. This required several hours. When dry, the plates were examined for uniformity of coating, and were boxed for future use. The grains on slides prepared in this manner are almost if not exactly in one plane." (*J. Phys. Chem.* **27**: 7-8. Jan., 1923.)

Wightman, Trivelli, and Sheppard⁸⁰ find that for one-grain-layer plates treatment with chromic acid prior to exposure, increases gamma-infinity.

Sheppard⁸¹ states that "Higson and Toy⁸² recall Sheppard and Mees's observation that desensitizing a plate with chromic acid increases gamma-infinity. This has recently been confirmed in this Laboratory, and it has also been found, by experiments with one-grain-layer plates, that the desensitizing action of chromic acid affects the smaller more than the larger grains. Consequently, the range of grain-sizes effective in exposure is reduced, and thereby gamma-infinity is increased."

Wightman and Sheppard⁸³ "have found that in certain emulsions a large part of the 'sensitivity' destroyed by chromic acid, can be regenerated by treatment with potassium iodide. This is quite analogous to the regeneration of the latent image by such nucleus exposure methods (due to Lüppo-Cramer) and points to the 'latent image' and 'sensitivity' being of like nature."

Sheppard, Wightman, and Trivelli⁸⁴ describe experiments relating to the effect of chromic acid in removing the fog produced by the action of dilute potassium iodide solution. They conclude that the experiments "do not give definite confirmation of the 'nucleus exposure' hypothesis. In particular, the treatment with chromic acid *after* iodizing did not markedly reduce the fogging action of this, while treatment with chromic acid *prior to* iodizing did. This result is possibly due to the chromic acid treatment, in the second case, interfering with the iodizing by tanning the gelatin. In any case, the results seem more consistent with the adsorption hypothesis." They summarize in a table their results "on the effect of chromic acid at different concentrations on (a) the latent image, (b) the sensitivity. These terms are used here formally, to signify that in case (a) the chromic acid, *etc.*, treatment was used *after* exposure, before development, and in (b) *before* exposure. In saying provisionally that the effect in case (a) exhibits the destruction of 'latent image,' this shall not be interpreted as meaning complete destruction, nor even as excluding paralysis of developability. Effectively, so much latent image is put out of action for a given type of development. Similarly, in case (b) any apparent or effective desensitizing may be due either

⁸⁰ E. P. Wightman, A. P. H. Trivelli, and S. E. Sheppard: *Trans. Faraday Soc.* **19**: 277. 1923 (Nov.).

⁸¹ S. E. Sheppard: *Colloid Symposium Monograph, University of Wisconsin* **357**. 1923.

⁸² G. I. Higson and F. C. Toy: *Phot. J.* **63**: 72. 1923 (Feb.).

⁸³ S. E. Sheppard: *Colloid Symposium Monograph, University of Wisconsin* 365-6. 1923.

⁸⁴ S. E. Sheppard, E. P. Wightman, and A. P. H. Trivelli: *J. Frank. Inst.* **196**: 661. 1923 (Nov.).

Action of Chromic Acid on Latent Image (a) and Sensitivity (b)

Treatment (5 minutes)	After- treatment	Degrees Chapman-Jones											
		Seed Graflex		Seed Lantern		Seed Process		News Bromide		Contrast Velox		Lippmann (washed)	
		173000		5400		5400		1320		6		1	
Blank	Blank	a	b	a	b	a	b	a	b	a	b	a	b
		25	25	25	25	25	25	25	25	25	25	25	25
CrO ₃ 5% H ₂ SO ₄ 1%	NaHSO ₃ 5%	0	0										
CrO ₃ 2 % H ₂ SO ₄ .5%	NaHSO ₃ 5%	0	19	0	14	0	15	0	15	18	25	0	25
CrO ₃ 1 % H ₂ SO ₄ .25%	NaHSO ₃ 5%	14	20										
CrO ₃ .5% H ₂ SO ₄ .125%	NaHSO ₃ 5%	15	22	0	17	0	18	15	17	20	25	0	25
CrO ₃ .25% H ₂ SO ₄ .06%	NaHSO ₃ 5%	16	23	0	20	0	18	19	19	21	25	0	25
Development.....		p.-a.-p. 4 mins.		p.-a.-p. 4 mins.		p.-a.-p. 4 mins.		p.-a.-p. 4 mins.		MQ 1 : 4 4 mins.		p.-a.-p. 15 mins.	

S* refers to relative sensitivity, in terms of Lippmann emulsion as 1.

to actual reduction of sensitivity prior to exposure, or to something remaining after the treatment, which destroys, or inhibits, the nascent 'latent image.' This latter possibility is largely discounted in the present case, because the after-treatment with bisulfite destroys any chromic acid, converting it to (a complex) chromium sulfate which, although it tans the gelatin, does not affect either sensitivity or appreciably inhibit development. This was determined by separate and special tests." "The question of removal or destruction of the oxidizer is of critical importance. When a plate is treated (A) before exposure, (B) after exposure, before development, the effects observed might be due to the following conditions:

A <i>Before Exposure</i>	B <i>After Exposure, Before Development</i>
(a) The oxidizer may destroy sensitizing nuclei.	The oxidizer may destroy the latent image.
(b) The oxidizer, remaining in the emulsion, may destroy the nascent latent image.	The oxidizer may inhibit the development, <i>e.g.</i> , <i>poison</i> the development centers.
(c) The oxidizer, remaining in the emulsion during and after exposure, may interact with the developer and reduce its concentration."	

"In most cases, for relatively short treatment with not too concentrated CrO_3 —up to 2 per cent—we find that a bath of 5 per cent NaHCO_3 , followed by good washing, is sufficient to remove the CrO_3 . For 'one-grain layers,' subsequently noted, this treatment is entirely adequate, but for ordinary emulsions the removal of CrO_3 must be tested." They⁸⁵ discuss the destruction and regeneration of both sensitivity and the latent image, with a detailed description of further experiments involving the action of baths of chromic acid with sulfuric acid and of ammonium persulfate with sulfuric acid on ordinary multi-grain-layer emulsions. Regarding the action of persulfate, a fogging effect was frequently observed. "Experiments with a silver chloride emulsion showed a much greater resistance of the *latent image* to persulfate than the bromo-iodide emulsion. As in the case of chromic acid, the reduction of *sensitivity* by persulfate could be completely annulled by a bisulfite bath; both bisulfite, and still more neutral sulfite, producing increase of sensitivity." In an investigation of the relation of chromic acid desensitizing to size of grain, the authors used a Seed Graflex emulsion coated in one-grain layers, and desensitized this with a solution of 0.5 per cent CrO_3 with 0.2 per cent H_2SO_4 , washing first with one per cent

⁸⁵ S. E. Sheppard, E. P. Wightman, and A. P. H. Trivelli: *J. Frank. Inst.* **196**: 779. 1923 (Dec.).

NaHCO_3 to help remove CrO_3 , then with one per cent hydrochloric acid to neutralize, and finally in several changes of distilled water. Untreated and treated plates were exposed and then developed in $M/10$ ferrous oxalate, the developed silver removed with chromic acid (0.5 of 1 per cent CrO_3 with 0.5 of 1 per cent H_2SO_4), and photomicrographs made. Blank controls with the NaHCO_3 , *etc.*, showed practically no difference from untreated plates. From the photomicrographs of the residual silver halide grains, size-frequency curves were constructed in different exposure steps. The authors conclude that the effect of chromic acid on sensitivity is greater for the small than for the large grains, but that this selectivity is diminished as the absolute exposure is increased. From the results of these and further experiments on sensitivity with the one-grain-layer plates, they conclude that "the 'sensitivity nuclei' are only incompletely removed by CrO_3 ... Subsequent action of KI and CrO_3 indicates that much of the sensitivity is occluded, and may be released by certain means. The action of iodide here is in good agreement with the part played by the 'latent image,' and points to a similar nature of the 'latent image' and 'sensitivity,' *viz.*, colloid silver. We regard this work as substantiating Lüppo-Cramer's 'Keimblosslegung' theory so far as relatively strong iodide solutions are concerned, but consider that with the very dilute solutions adsorption effects are more important."

For the removal of emulsion fog from plates, Lüppo-Cramer recommends⁸⁶ the use of a more dilute acidified potassium dichromate solution than that prescribed by Eder. The plates may be bathed in a solution of two grams of potassium dichromate and 4 c.c. of concentrated sulfuric acid in 1 liter of water, for 1.5 minutes, and the chromic acid removed by a bisulfite bath, or an unacidified 2 per cent potassium dichromate solution may be used, the plates being immersed for 5 - 10 minutes. In either case, the latent emulsion fog is effectively removed, while sensitivity is not so greatly diminished as by Eder's solutions.

Clark⁸⁷ continues his experiments on the effect of chromic acid on sensitivity, using both multi-grain-layer plates and single-grain-layer plates prepared from a process emulsion. He summarizes his results as follows:—"The action of chromic acid on a single-layer plate is to bring about a general lateral shift of the characteristic curve of the plate. The gamma is unaltered if sufficient treatment with desensitizer be given, but the total range of the curve is decreased owing to decrease

⁸⁶ Lüppo-Cramer: *Über den latenten Schleier*. *Z. angew. Chem.* **37**: 46. 1924 (Jan. 24).

⁸⁷ W. Clark: *Phot. J.* **64**: 91-6. 1924 (Feb.).

in the range of the fully exposed portion. The general increase in gamma brought about by treating a finished plate with chromic acid is due to the range decrease in the sensitivities of each grain-size class. In an emulsion, for a given treatment, the smaller grains are relatively more desensitized by chromic acid than are the larger grains. The minimum speeds attained by treatment of ultra-rapid, special rapid, and process plates by chromic acid are 5, 2, and 1 H. and D., respectively. Exposure to light before desensitization increases the rate of decrease of sensitivity, the effect being more marked with 'ultra-rapid' plates than with those of 'special rapid' type, and absent in the case of 'process' plates. . . . Treatment of grains with chromic acid lowers the ratio of the number of reduction centers formed on the edges of the grains, compared with the number on the flat surface."

Engelken⁸⁸ recommends the following procedure for the removal of latent fog from old gelatin emulsion plates so that they may be available for use in photomicrography. Bathe for 1 minute in a solution of 5 grams of potassium dichromate and 10 c.c. of concentrated sulfuric acid in 1 liter of water; rinse the plate front and back, bathe for 1 minute in 1 : 100 rodinal; rinse as before; bathe for 3 minutes in a mixture of 1 part of alcohol and 2 parts of water; and dry in the dark. By this treatment the general sensitivity of the plates used was reduced to about one-third. By adding a suitable dye, however, to the bath of dilute alcohol, color-sensitivity could readily be obtained.

Milbauer and Flek⁸⁹ find that dilute (about 0.01 per cent) solutions of chlorine, bromine, or iodine, lessen the edge- and general fog of old plates, but do not alter the gradation. The following method is recommended for the removal of fog from old plates:—Bathe for 15 minutes in a 0.25 per cent hypo solution; bathe for 4 minutes in a 1 per cent potassium persulfate solution; wash for 15 minutes in running water; remove the surface moisture; and dry in a current of air. Sensitivity is reduced to about one-ninth.

Lüppo-Cramer⁹⁰ finds, in the case of light-exposed "lantern" plates, that preliminary bathing in a 0.5 per cent sodium hydroxide solution for 3 minutes, followed by thorough washing and drying, has the effect of hastening or increasing the destroying action of a subsequent 2 per cent potassium dichromate bath on the previously impressed latent image. Compared

⁸⁸ H. Engelken: *Phot. Rund.* **61**: 21. 1924 (Feb.).

⁸⁹ J. Milbauer and J. Flek: Über die Nutzbarmachung des alten photographischen Plattenmaterials. *Phot. Rund.* **61**: 45. 1924 (March).

⁹⁰ Lüppo-Cramer: *Phot. Ind.* **22**: 188. 1924 (March 26).

with plates that had not received the preliminary alkali treatment, a loss of latent image corresponding to more than 10 degrees Eder-Hecht was observed.

Ninck⁹¹ recommends the following treatment prescribed in the *Agenda Lumière* for removal of fog prior to hypersensitization from autochromes fogged by age: bathe the plates for 5 minutes in a solution of 0.5 per cent chromic acid with 1 per cent potassium bromide, and wash for 5 minutes.

Sheppard, Wightman, and Trivelli⁹² describe experiments on the desensitizing effect of copper sulfate solution on single-grain-layer plates prepared from a Seed Graflex emulsion. Unlike ordinary plates, the single-grain-layer plates show an increase in gamma-infinity, the maximum density, however, being reached at about the same exposure for treated and untreated plates. It is suggested in explanation of the desensitizing action of copper sulfate in the presence of the traces of soluble halide that "if the theory of pre-exposure nuclei is correct and these nuclei consist of colloidal silver particles, then when copper sulfate is added, we may have a reduction of this to cuprous salt and an oxidation of the silver nucleus to silver halide. That is to say, the same action is possible in regard to 'sensitivity nuclei' as previously supposed by Mees and Sheppard in regard to the latent image by retained copper salt. The cuprous salt could then be aerially oxidized and become again effective." In a study of the action of chromic acid on ordinary multi-grain-layer plates, with various times of treatment the authors find that gamma is greatly reduced, and considerable destruction of the latent image occurs, this destruction increasing with increasing time of treatment until almost no image is developable except at an exposure nearly 3800 times that of the untreated plate. Even at 36,000 times, after a comparatively short treatment, the densities produced are very low compared with those of the untreated plates. The appearance of an image after the treatment is explained by the difficulty of removing the last traces of latent image, and it may be equally difficult to remove the last traces of sensitivity nuclei.

Lüppo-Cramer⁹³ exposes a fine-grained silver bromide lantern plate behind a Chapman-Jones tablet until the first fields are directly visible, bathes this in 1/10th saturated bromine water for 5 - 10 minutes, washes thoroughly, and dries. On chemical, or on post-fixation physical, development, no trace

⁹¹ Ninck: *Rénovation des autochromes périmées. Bull. soc. franç. phot.* **11**: 83. 1924 (April).

⁹² S. E. Sheppard, E. P. Wightman, and A. P. H. Trivelli: Desensitizing with Copper Salts. *J. Frank. Inst.* **198**: 511. 1924 (Oct.).

⁹³ Lüppo-Cramer: *Phot. Ind.* **22**: 982. 1924 (Nov. 3).

of image can be found; but if, instead of developing, a uniform exposure to daylight is given, the image that was visible before treating with bromine again slowly makes its appearance, and after several days' exposure is not lost in general fog, but may be permanently retained by fixing. Lüppo-Cramer suggests that the silver bromide re-formed by the action of bromine, no longer possesses its original crystal structure, but is more or less disintegrated, as in the somewhat similar case of the action of a dilute solution of a soluble iodide ("Keimblosslegung" effect). Using a different and more complicated procedure, which also results in the conversion of small fractions of the silver halide of an emulsion into silver bromide, the writer observed a differentially higher sensitivity of newly formed silver bromide for ordinary exposure to light and chemical development. This effect is possibly related to that described by Lüppo-Cramer.

Lüppo-Cramer⁹⁴ states that, generally, the higher the light-sensitivity of a plate, other things being equal, the greater is the regression of sensitivity on treatment with chromic acid. He finds that in making an emulsion by the "boiling" method, after there is no further appreciable increase in the average grain-size, the sensitivity may be increased 20 or 30 times by continued heat treatment. The effect of chromic acid treatment is now to reduce both the partly ripened and fully ripened emulsions, and also one that had been over-ripened to complete fogging, to approximately equal sensitivity. This is true for ordinary chemical, and also for physical, development.

Ross⁹⁵ discusses reduction of sensitivity by copper sulfate, and by chromic acid, and describes new experiments. Using Eastman 33 plates and one per cent copper sulfate solution, for development in an MQ process developer for 5 minutes at 70° F., he varies the times of bathing and subsequent washing. "The effect of washing in water after the desensitizing bath is pronounced, the action being notably reduced. Of equal interest is the effect on gamma or contrast, short bathing (10 sec.) giving a marked increase compared with the unbathed data. For a three-minute bath, the contrast is equal to that of the unbathed plate, while prolonged bathing, without subsequent washing, results in a further reduction. In all cases, washing the plate increases the contrast. . . . In the case of plates treated for 10 seconds, a notable decrease in fog was observed. . . . With longer bathing times or greater concentration of the copper sulfate, especially if the plate is not washed after the

⁹⁴ Lüppo-Cramer: *Z. wiss. Phot.* **23**: 86-7. 1924 (Dec.).

⁹⁵ F. E. Ross: *Brit. J. Phot.* **72**: 5-6. 1925 (Jan. 2).

desensitizing bath, an increase in fog is obtained." In a further series of experiments, in which a 5 per cent concentration of copper sulfate is used, the effect of washing the bathed plate respectively before and after exposure is observed. For an unwashed plate speed reduction is greatest, but contrast is low and fog excessive. If high contrast is not needed, washing before development is recommended because of the low value of fog and high degree of desensitizing. With reference to desensitization by means of chromic acid, Ross⁹⁶ says:—"On account of its strong oxidizing power, chromic acid will destroy the latent image as well as act as a desensitizer. Its desensitizing power is very great if the excess is not washed out of the emulsion before exposure. Thus bathing for 3 minutes in an 0.5 per cent solution without subsequent washing may reduce the sensitivity 10,000 times. With a strength one-third of this, the reduction is but 120 times." The effects of interposing between exposure and development, the operations of washing for 1 minute, bathing in 0.5 per cent chromic acid for 2 minutes, and washing again for 1 minute, are shown by comparative density curves of an untreated and a treated plate. Increasing exposure shows first a complete loss of latent image, then a lowering of gamma, and finally an increase of gamma. The effect of the obtaining by this means of an ascending series of densities in the solarizing region of exposure [as observed in 1902 by Eder³⁸] is clearly shown. Ross remarks that we "are apt to look upon the over-exposure region, or on over-exposed plates, as valueless. . . . The writer exposed two films on an outdoor subject, one of normal exposure, the second 150 times normal. The latter, before development, was bathed for 1 minute in 0.5 per cent chromic acid, then 3 minutes in water. The two negatives were nearly identical."

Arens,⁹⁷ in a dissertation "on the interpretation of photographic reversal phenomena," describes experiments on the action of dilute solutions of potassium dichromate with excess of sulfuric acid, followed by washing, on latent light-images extending into what is the solarizing region for direct ordinary chemical development. (The sensitive material, presumably a silver halide gelatin emulsion, is referred to only as "the plate"; development was apparently in all cases with hydroquinone, but details are not given, nor any experiment showing the effect of varying the degree of development.) In the conclusion, Arens writes: "The end result of the chromic acid treatment may now be decided very easily. We have finally in the solarization region a rising density curve, but one which

⁹⁶ F. E. Ross: *Brit. J. Phot.* **72**: 19. 1925 (Jan. 9).

⁹⁷ H. Arens: *Z. physik. Chem.* **114**: 343-53. 374. 1925 (Jan. 20).

is derived from a [kind of] silver that is more difficultly developable than the original solarization image." Later, he describes experiments in which similar acid dichromate solutions were used in an investigation of the Villard and Herschel effects.

Lüppo-Cramer⁹⁸ cites several instances of the formation of fog by oxidizing agents capable of destroying a latent light-image and of bleaching a developed silver image. He mentions his old experience with ammonium persulfate²⁴ and with bromine water,³⁷ and the recent experience of Sheppard, Wightman, and Trivelli with solutions of ammonium persulfate with sulfuric acid [*J. Frank. Inst.* **196**: 784. 1923 (Dec.)], and he describes later experiments showing the fogging action of chromic acid with potassium bromide, and of neutral or weak alkaline ammonium persulfate with potassium bromide, on a neutral-ripened emulsion.

Lüppo-Cramer⁹⁹ states that a lantern plate, which has been treated with chromic acid mixture after exposure, then thoroughly washed and bathed in 1 per cent potassium iodide solution for 30 seconds, and washed, gives a vigorous image in the physical developer, while without the iodide treatment it gives no trace of image in 30 minutes. He finds¹⁰⁰ that a latent image on plates coated with an emulsion that has been ripened by boiling, and then bathed in caustic soda, is more extensively (20° or 30° Eder-Hecht) destroyed by a dilute dichromate solution than is the latent image on similar plates that have not received the soda treatment.

Lüppo-Cramer¹⁰¹ finds that the sensitivity of a heat-ripened Lippmann emulsion containing 3 per cent silver iodide is reduced about 36° Eder-Hecht by treatment with chromic acid mixture, while the sensitivity of the unripened emulsion is scarcely affected. The difference in sensitivity between the ripened and unripened emulsion, after the chromic acid treatment, is 30° in favor of the ripened.

Carroll,¹⁰² in connection with photography in the infra-red by reversal, records experiments which bear some resemblance to those of Abney, in 1881, which were, however, with wet collodion. Seed 23 and Process plates were given an optimum exposure to white light, bathed in solutions of oxidizing agents, rinsed, dried, and exposed in a spectrograph. "Ferric chloride, potassium ferricyanide and potassium dichromate in 0.05 per

⁹⁸ Lüppo-Cramer: Ueber Schleierbildung durch Oxydationsmittel. *Phot. Ind.* **23**: 291. 1925 (March 16).

⁹⁹ Lüppo-Cramer: *Z. wiss. Phot.* **23**: 123. 1925 (April).

¹⁰⁰ Lüppo-Cramer: *Z. wiss. Phot.* **23**: 128. 1925 (April).

¹⁰¹ Lüppo-Cramer: *Z. wiss. Phot.* **23**: 227-8. 1925 (June).

¹⁰² B. H. Carroll: *J. Phys. Chem.* **29**: 696-702. 1925 (June).

cent solution, potassium permanganate in 0.02 per cent, and nickel nitrate in 0.05 per cent solution, caused no reversal. Cupric salts appeared to be particularly promising, as they have an absorption band in the red and short infra-red with maximum at about 0.8μ , are photochemically sensitive, acting as oxidizing agents, and are strong photographic desensitizers. In the first experiments, pre-exposed plates were bathed in 0.1 per cent cupric chloride or bromide, followed by or mixed with 1 per cent potassium bromide. The latent image was totally destroyed without exposure; the plates after developing and fixing were glass clear. Sensitivity was greatly diminished, but not destroyed, as a direct image was obtainable on such plates in the region of sensitivity of the untreated plate. An attempt to reduce the copper ion concentration by using an ammoniacal solution produced only fog, but when 0.04 per cent cupric tartrate or 0.1 per cent cupric acetate was used, reversal appeared between 0.67 and 0.88μ . The tendency to destroy the latent image in the dark was still strong, and was greatly increased by bathing with potassium bromide after the copper salt. The pH of the copper tartrate solution was lowered to 2.5 by addition of tartaric acid, without noticeable effect; addition of ammonia caused fog. In all cases, the latent image faded rapidly after bathing with the copper salts. When their concentration was sufficiently low, their activity in the dark was correspondingly reduced, so that the effects of the reversing exposure became evident, but no salt or combination of salts was found which combined stability of the bathed plates in the dark with reversal over the entire absorption band of copper in the light. The photochemistry of copper salts should have further study as possible sensitive materials for infra-red photography. Further experiments with ferric salts were successful to the extent of securing a faint reversal around 0.6μ on a process plate bathed with ferric oxalate. Bathing with 0.1 per cent mercuric chloride caused complete destruction of latent image in the dark and apparently complete desensitization." Presumably, the plates were *merely* rinsed between the chemical treatment and the second exposure. In Abney's experiments, at this stage, no washing was given; and in Carroll's earlier experiments using dyes, only rinsings were given, and if this is so in the present experiments, it is clear that much of the oxidizer remained in the film and was there during the second exposure, and the desensitization observed must be far in excess of the permanent effect of sensitivity-diminution on the emulsion.

A. Rossi,¹⁰³ in reference to the removal of stain from the

¹⁰³ A. Rossi: *Riv. fot. ital.* 8: 109. 1923.

gelatin film when safranin has been used as a desensitizer, states that decoloration with an acidified solution of potassium or sodium nitrite is open to the objection that a certain amount of reduction of the image may occur.

L. J. G. van Ewijk and H. J. Prins¹⁰⁴ have been granted an English patent (231246) for a process which, "in contradistinction to the known reversal processes, produces a positive image on photographic plate or film by exposing and developing the negative image (without fixing), *then effecting the secondary exposure through the primary negative image on the same sensitive layer*, removing the negative image by bleaching, and finally developing and fixing the secondary positive image."

Kögel and Steigmann¹⁰⁵ remark that the desensitizing effect of mercuric salts is so tremendous that the photographic developing-out emulsion may well be regarded as the finest reagent for the detection of traces of mercuric ion in extremely dilute solutions.

Reychler¹⁰⁶ describes the action, for post-fixation physical development, of a solution of chromic acid, potassium bromide and sulfuric acid, on a latent image on a photographic plate, before fixing, and between fixing and developing. He finds that an application of the bromidizing bath before fixing allows the development of a fair image, only the lowest light-exposures being impaired, whereas when applied after fixing not more than a trace of image can be developed. Reychler concludes that the nuclei produced by the action of light are distributed not only on the surface but also through the depth of the silver halide grain, and that only the surface nuclei are quickly attacked by the bromidizing bath, while the interior nuclei that survive this treatment are effective, after fixing, for physical development. The writer, however, from his experience of the action of solutions of relatively high oxidation potential, would not have expected nearly so considerable a survival of latent image, after treatment between exposure and fixation. Following Reychler's procedure as closely as the description allows, Eastman Slow Lantern and Speedway plates, as examples of emulsions differing widely in silver halide grain-size, were treated with a bromidizing bath of CrO_3 , 1.5 grams; KBr , 0.75 gram; H_2SO_4 , 0.30 gram; water, to 100 c.c.; washed, treated or not treated with dilute sodium bicarbonate solution, fixed in slightly ammoniacal 15 per cent

¹⁰⁴ L. J. G. van Ewijk and H. J. Prins: *Brit. J. Phot.* **72**: 523-4. 1925 (Aug. 28).

¹⁰⁵ G. Kögel and A. Steigmann: *Phot. Ind.* **23**: 1065. 1925 (Sept. 28).

¹⁰⁶ A. Reychler: Le développement physique de l'image latente. *Bull. soc. chim. Belg.* **35**: 74. 1926 (Feb.).

hypo solution, washed in changes of water containing ammonia, and developed (up to 24 hours) in a mercury sulfite physical developer. A destruction of latent image extending through the "underexposure" into the "correct exposure" region after five minutes' treatment of Eastman Speedway and five to fifteen minutes' treatment of Eastman Slow Lantern emulsion, at 20° C., was observed. It appears safe to conclude that, with the particular $\text{CrO}_3\text{-KBr-H}_2\text{SO}_4$ bath used, which is of the mean composition stated by Reychler, it is only a matter of duration of time of action before the latent image on any emulsion will be completely destroyed for any kind of development. This is in harmony with the suggestion offered in Chapter II (p. 84) that a solution of relatively high oxidation potential is able to remove the silver sulfide sensitivity nuclei of a silver halide grain and so gain access to and destroy the sub-surface latent image.

The authority and year in the second and third columns respectively, in the following table, are those of the earliest reference directly accessible and are not necessarily the original author and date of observation. This is a review of the literature up to September, 1926.

Perhaps the most interesting single question in regard to the nature of the latent image is whether it is, or is not, identical in the daguerreotype, collodion, and gelatin processes. Bromine, or bromine water, has been observed to destroy the latent image in all three cases. In addition, chlorine, chromic acid, cupric bromide, cupric chloride, ferric bromide, mercuric chloride, mercuric nitrate, nitrous acid, potassium dichromate and potassium ferricyanide have been observed to destroy the latent image in both the collodion and gelatin processes. No instance of the destruction of the latent image in any one process, and absence of any loss of the latent image in another, by the same chemically oxidizing solution, has been verified, as far as the writer is aware. These data, while not proving, suggest, the identity of the latent image in the three processes, and, further, they are not inconsistent with the view that it is composed of silver. The general experience that, under similar conditions, the latent image of silver iodide is more easily destroyed by oxidizing agents than that of silver bromide, and this again than that of silver chloride, is seen, if the chemistry of the reactions is considered (see Chapter IV, pp. 108-9), to be in harmony with the silver theory.

A Summary of the Literature on the Action of Silver-Oxidizing Baths on Sensitivity and on the Latent Image.

Chemical Agent(s) (in solution in water)	Authority	Year	Material or Process	Means of formation of latent image (or fog)	Effect of bath on latent image (or fog)	Effect of bath on sensitivity to light	Reference Number
Ammonium persulfate	Lüppo-Cramer	1901	Collodion emulsion	Light	Not entirely destroyed	Reduced to about one-half	25
Ammonium persulfate	Lüppo-Cramer	1901	Bromide gelatin emulsion		Fog produced		24
Ammonium persulfate	K. Schaum and W. Braun	1902		Light	Destroyed: latent image of <i>solarizing</i> exposures converted into one that develops normally		33
Ammonium persulfate	Lüppo-Cramer	1909	High-speed gelatin emulsion	Light	Reversed if treatment is followed by washing and brief uniform exposure		58
Ammonium persulfate, with potassium bromide (neutral or feebly alkaline)	Lüppo-Cramer	1925	Ripened gelatin emulsion	Light	Fog produced		98
Ammonium persulfate, with sulfuric acid	S. E. Sheppard, E. P. Wigman, and A. P. H. Trivelli	1923	High-speed gelatin emulsion, and gelatino-chloride emulsion	Light	Destroyed as regards lowest exposures. Fog frequently produced	Reduced, but regained by treatment with sulfite or bisulfite	85
Auric chloride	J. M. Eder	1903	Gelatino-bromide emulsion	Light	Destroyed		40
Auric chloride	B. Homolka	1903	High-speed gelatin emulsion	Light	Developed		42
Auric chloride, with phosphoric acid	B. Homolka	1903	Bromide gelatin emulsion, and gelatin and collodion P.O.P.	Light	Developed		42
Auric chloride	S. E. Sheppard and C. E. K. Mees	1907	Gelatin emulsion	Light	Developed		52
Bromine	G. Wardley	1862	Daguerreotype	Light	Destroyed	"Restored"	3
Bromine	W. de W. Abney	1877	Collodio-bromide emulsion	Light	Destroyed		6

Summary—continued

Chemical Agent(s) (in solution in water)	Authority	Year	Material or Process	Means of formation of latent image (or fog)	Effect of bath on latent image (or fog)	Effect of bath on sensitivity to light	Reference Number
Bromine	J. M. Eder	1895	Collodio-bromide emulsion	Light	Destroyed		14
Bromine	J. Sterry	1898	Gelatin emulsion	Light	"To delay reversal"	"To delay reversal"	19
Bromine	E. Englisch	1899	Gelatin emulsion, and collodion emulsion plates	Light	Destroyed	Reduced enormously	21
Bromine	Lüppo-Cramer	1900	Gelatin emulsion	Light	Destroyed	Reduced enormously	24
Bromine	Lüppo-Cramer	1900	Collodion emulsion	Light	Destroyed	Reduced to about $\frac{1}{4}$ th	24
Bromine	Lüppo-Cramer	1901	Collodion	Light	After fixation, destroyed for physical development	After fixation, recreated but in very low degree (for physical development)	27
Bromine	Lüppo-Cramer	1902	Gelatin emulsion	Emulsion or storage	Not removed		30
Bromine	Lüppo-Cramer	1902	Gelatin emulsion	Light	Partially destroyed	Reduced	30
Bromine	Lüppo-Cramer	1902	Gelatino-bromide emulsion	X-rays	Destroyed		31
Bromine	Lüppo-Cramer	1902	Gelatin emulsion	Storage	Wholly unaffected		32
Bromine	Lüppo-Cramer	1902	Gelatin emulsion	Impact	Destroyed		32
Bromine	J. M. Eder	1902	Gelatin emulsion, and collodion emulsion	Light	Destroyed: latent image of <i>solarizing</i> exposures converted into one that develops normally, this also being destroyed by protracted treatment		33
Bromine	Lüppo-Cramer	1903	High-speed gelatin emulsion	Emulsion or storage	Not destroyed, but actually somewhat increased		37
Bromine	Lüppo-Cramer	1903	Low-speed gelatin emulsion	Emulsion or storage	Destroyed		37

Summary—continued

Chemical Agent(s) (in solution in water)	Authority	Year	Material or Process	Means of formation of latent image (or fog)	Effect of bath on latent image (or fog)	Effect of bath on sensitivity to light	Reference Number
Bromine	J. M. Eder	1903	Gelatino-bromide emulsion	Emulsion or storage, and light	Destroyed		41
Bromine	J. M. Eder	1903	Gelatino-bromide emulsion	Emulsion or storage, and light	Tendency to, or actual, destruction, when added to emulsion in preparation	Lowered	43
Bromine	J. Sterry	1907	Gelatin emulsion	Light	In part changed into a less, or non-developable condition		53
Bromine	F. Kropf	1919	Gelatin emulsion	Emulsion or storage	Destroyed in rare cases only, in most cases unaffected, and sometimes actually increased		64
Bromine	J. Milbauer and J. Flek	1924	High-speed gelatin emulsion	Emulsion or storage	Reduced	(Gradation unaltered)	89
Bromine oxyacids	J. M. Eder	1895	Collodion emulsion	Emulsion or storage	Destroyed		16
Chloric acid	J. M. Eder	1903	Gelatino-bromide emulsion	Emulsion or storage, and light	Tendency to, or actual destruction when added to emulsion in preparation	Lowered	43
Chlorine	J. M. Eder	1895	Collodio-bromide emulsion	Light	Destroyed		14
Chlorine	J. M. Eder	1903	Gelatino-bromide emulsion	Emulsion or storage, and light	Destroyed		41
Chlorine	J. M. Eder	1903	Gelatino-bromide emulsion	Emulsion or storage, and light	Tendency to, or actual, destruction when added to emulsion in preparation	Lowered	43
Chlorine	R. A. Reiss	1903	Gelatin emulsion		Fog produced		44
Chlorine	J. Milbauer and J. Flek	1924	High-speed gelatin emulsion	Storage	Reduced	(Gradation unaltered)	89

Summary—continued

Chemical Agent(s) (in solution in water)	Authority	Year	Material or Process	Means of formation of latent image (or fog)	Effect of bath on latent image (or fog)	Effect of bath on sensitivity to light	Reference Number
Chlorine-liberating mixtures	J. M. Eder	1903	Gelatino-bromide emulsion	Emulsion or storage, and light	Tendency to, or actual, destruction when added to emulsion in preparation	Lowered	43
Chlorine oxyacids	J. M. Eder	1895	Collodion emulsion	Emulsion or storage	Destroyed		16
Chromic acid	W. de W. Abney	1877	Collodio-bromide	Light	Destroyed		8
Chromic acid	W. de W. Abney	1877	Collodio-iodide	Light	Destroyed		8
Chromic acid	W. B. Bolton	1884	Gelatin emulsion	Light	Destroyed		10
Chromic acid	Lüppo-Cramer	1902	Gelatino-bromide emulsion	X-rays	Destroyed		31
Chromic acid	J. M. Eder	1902	Gelatino-bromide emulsion	Light	Destroyed: latent image of gelatin, exposures converted into one that develops normally		33
Chromic acid	S. E. Sheppard and C. E. K. Mees	1907	Gelatin emulsion	Light	Destroyed (as shown logically by exact experiments and density measurements)		49
Chromic acid	J. Sterry	1907	Gelatin emulsion	Light	In part changed into a less, or non-, developable condition		53
Chromic acid	Lüppo-Cramer	1909	High-speed gelatin emulsion	Light	Reversed if treatment is followed by washing and brief uniform exposure		58
Chromic acid	Lüppo-Cramer	1915	Collodion emulsion, prepared without any addition of chemically reducing substance			Unaffected	62
Chromic acid	Lüppo-Cramer	1915	Ripened gelatin emulsion			Greatly reduced	62

Summary—continued

Chemical Agent(s) (in solution in water)	Authority	Year	Material or Process	Means of formation of latent image (or fog)	Effect of bath on latent image (or fog)	Effect of bath on sensitivity to light	Reference Number
Chromic acid	F. F. Renwick	1920	Collodion emulsion	Light	Reversed if treatment is followed by washing and brief uniform exposure		66
Chromic acid	S. E. Sheppard	1922	All gelatin emulsions			Reduced	72
Chromic acid	W. Clark	1923	Gelatin emulsion	Light	(Not mentioned whether completely destroyed under the experimental conditions)	Reduced, this reduction being greatly accelerated by preliminary brief exposure to light	77 78
Chromic acid	S. E. Sheppard, A. P. H. Trivelli, and E. P. Wightman	1923	High-speed gelatin emulsion, re-coated, in single-grain layer	Light	Destroyed: latent image of solarizing exposures converted into one that develops normally	Reduced in the "toe" of the curve relatively more than in other parts. (If not washed out before exposure, desensitized completely)	79
Chromic acid	E. P. Wightman, A. P. H. Trivelli, and S. E. Sheppard	1923	High-speed gelatin emulsion, re-coated in single-grain layer			Gamma-infinity increased	80
Chromic acid	S. E. Sheppard	1923	Certain gelatin emulsions			Reduced, part of the loss being regainable by treatment with potassium iodide	83
Chromic acid	S. E. Sheppard, E. P. Wightman, and A. P. H. Trivelli	1923	Gelatino-bromide emulsion	Dilute potassium iodide solution	Not markedly reduced		84
Chromic acid	W. Clark	1924	Gelatin emulsions	Light	(Not mentioned whether completely destroyed under the experimental conditions)	Reduced to 5 (H. and D.) in case of "ultra-rapid," to 2 in case of "special rapid," and unchanged at 1 in case of "process," plates	87

Summary—continued

Chemical Agent(s) (in solution in water)	Authority	Year	Material or Process	Means of formation of latent image (or fog).	Effect of bath on latent image (or fog)	Effect of bath on sensitivity to light	Reference Number
Chromic acid	W. Clark	1924	Low-speed gelatin emulsion, re-coated in single-grain layer			Reduced, although gamma is unaltered if sufficient treatment be given	87
Chromic acid	Lüppo-Cramer	1924	Gelatin emulsion			A partly- and fully-ripened emulsion are both reduced to approximately the same sensitivity, for either chemical or physical development	94
Chromic acid	F. E. Ross	1925	Medium-speed gelatin emulsion plates	Light	Destroyed: Eder's observation (ref. 33) regarding action on solarizing exposures confirmed	Very greatly reduced if not washed out before exposure	95
Chromic acid mixture	Lüppo-Cramer	1925	Gelatin "lantern" plate	Light	Not destroyed, for physical development, if followed by KI solution		99
Chromic acid mixture	Lüppo-Cramer	1925	"Lippmann" gelatin emulsion			Sensitivity of heat-ripened emulsion is greatly lowered, while that of unripened emulsion is scarcely affected	101
Chromic acid, with potassium bromide	Ninck	1924	Gelatin emulsion (auto-chrome plates)	Storage	Destroyed	The panchromatic, but not the blue, sensitivity destroyed	91
Chromic acid, with potassium bromide	Lüppo-Cramer	1925	Ripened gelatin emulsion	Light	Fog produced		98

Chemical Agent(s) (in solution in water)	Authority	Year	Material or Process	Means of formation of latent image (or fog)	Effect of bath on latent image (or fog)	Effect of bath on sensitivity to light	Reference Number
Chromic acid, with potassium bromide and sulfuric acid	A. Reyckler	1926	Gelatin emulsion plates	Light	Only the lowest light-exposures impaired when applied before fixing, for mercury physical development, while all but a trace of image destroyed when applied between fixing and developing		106
Chromic acid, with sulfuric acid	S. E. Sheppard, E. P. Wightman, and A. P. H. Trivelli	1923	Various gelatin emulsions	Light	Destroyed in all cases as regards lower light-exposures	Reduced in most cases; unaffected, however, with Contrast Velox and Lippmann emulsion	84
Chromic acid, with sulfuric acid	S. E. Sheppard, E. P. Wightman, and A. P. H. Trivelli	1923	Gelatin emulsion	Light	Destroyed as regards lower light-exposures	Reduced, but regained by treatment with sulfite or bisulfite	85
Chromic acid, with sulfuric acid	S. E. Sheppard, E. P. Wightman, and A. P. H. Trivelli	1923	High-speed gelatin emulsion, re-coated in single-grain layer			Reduced, more for the larger than for the smaller grains, but this selectivity diminishes as the absolute exposure increases	85
Chromic acid, with sulfuric acid	S. E. Sheppard, E. P. Wightman, and A. P. H. Trivelli	1924	High-speed gelatin emulsion	Light	Destruction nearly complete at 4000 times the Schwellenwert for untreated plates, and above this the densities produced are very low		92
Cupric bromide	J. T. Taylor	1877	Collodion emulsion	Light	Destroyed		5
Cupric bromide	W. de W. Abney	1877	Collodio-bromide emulsion	Light	Destroyed		6

Summary—continued

Chemical Agent(s) (in solution in water)	Authority	Year	Material or Process	Means of for- mation of latent image (or fog)	Effect of bath on latent image (or fog)	Effect of bath on sensitivity to light	Reference Number
Cupric bromide	B. H. Carroll	1925	Medium- and low- speed gelatin emulsion	Light	Totally destroyed	Greatly diminished, but not destroyed, when (pre- sumably) followed by brief washing	102
Cupric chloride	J. T. Taylor	1877	Collodion emulsion	Light	Destroyed		5
Cupric chloride	W. de W. Abney	1885	Gelatin emulsion	Emul- sion or light	Destroyed	Diminished slightly	11
Cupric chloride	Lüppo-Cramer	1901	Collodion emulsion	Light	Impaired	Somewhat impaired	25
Cupric chloride	J. M. Eder	1903	Gelatino- bromide emulsion	Emul- sion or storage, and light	Tendency to, or actual, destruction when added to emulsion in prepara- tion	Lowered	43
Cupric chloride	Lüppo-Cramer	1907	Gelatin emulsion	Light <i>vs.</i> emul- sion or storage	The light- image is destroyed before the fog. With certain con- centrations, fog is increased		59
Cupric chloride followed by KBr	B. H. Carroll	1925	Medium- and low- speed gelatin emulsion	Light	Totally destroyed	Greatly diminished, but not destroyed, when (pre- sumably) followed by brief washing	102
Cupric chlo- ride, with ammonia	A. Lumière and L. Lumière	1887	Gelatin emulsion	Light	Destroyed		13
Cupric salts	S. E. Sheppard and C. E. K. Mees	1907	Gelatin emulsion			Diminished	50
Cupric sulfate	S. E. Sheppard and C. E. K. Mees	1907	Gelatin emulsion	Light	Destroyed	Diminished	50
Cupric sulfate	F. C. Jordan and K. Burns	1921	Gelatin emulsion			Reduced to about 1/50 (washing after treat- ment, is omitted)	71

Summary—continued

Chemical Agent(s) (in solution in water)	Authority	Year	Material or Process	Means of formation of latent image (or fog)	Effect of bath on latent image (or fog)	Effect of bath on sensitivity to light	Reference Number
Cupric sulfate	Lüppo-Cramer	1922	Certain gelatin emulsions		Fog produced by bathing in freshly prepared dilute solution, and drying	Diminished greatly	75
Cupric sulfate	S. E. Sheppard, E. P. Wightman, and A. P. H. Trivelli	1924	High-speed gelatin emulsion, re-coated in single-grain layer			Gamma-infinity is increased; maximum density, however, is reached at about same exposure as for untreated plate	92
Cupric sulfate	F. E. Ross	1925	Medium-speed gelatin emulsion plates	Light	With brief following washing, some fog is produced	Reduced, the reduction being greater the higher the concentration and the longer the immersion, and less with following washing	95
Ferric ammonium citrate	Lüppo-Cramer	1922	Certain gelatin emulsions		Fog produced by bathing in freshly prepared dilute solution, and drying	Diminished greatly	75
Ferric bromide	W. de W. Abney	1877	Collodion-bromide emulsion	Light	Destroyed		6
Ferric chloride	R. Luther	1899		Light	Destroyed, according to Wetzlar and Carey Lea; not destroyed, according to Luther		22
Ferric chloride	Lüppo-Cramer	1901	Collodion emulsion	Light	Destroyed	Reduced to between 1/8th and 1/6th	25
Ferric chloride	J. M. Eder	1901	Gelatin emulsion	Emulsion or storage, and light	Tendency to, or actual destruction, when added to emulsion in preparation	Lowered	43

Summary—continued

Chemical Agent(s) (in solution in water)	Authority	Year	Material or Process	Means of formation of latent image (or fog)	Effect of bath on latent image (or fog)	Effect of bath on sensitivity to light	Reference Number
Ferric chloride	Lüppo-Cramer	1907	Gelatin emulsion	Light <i>vs.</i> emulsion or storage	The light-image is destroyed before the fog. With certain concentrations, fog is increased.		59
Ferric chloride	Lüppo-Cramer	1922	Certain gelatin emulsions	Light	Fog <i>produced</i> by bathing in freshly prepared dilute solution, and drying	Diminished greatly	75
Ferric oxalate	S. E. Sheppard and C. E. K. Mees	1907	Gelatin emulsion	Light	Not destroyed		51
Ferric salts	S. E. Sheppard and C. E. K. Mees	1907	Gelatin emulsion			Diminished	50
Gold chloride (see <i>Auric chloride</i>)							40 42 52
Hypo-bromous acid	G. A. Perley	1909 1910	Low-speed gelatin emulsion			Tendency towards solarization, checked	59 60
Iodine	G. Shadbolt	1861	Wet collodion, and albuminized collodion	Light	Destroyed		1
Iodine	J. T. Taylor	1862	Daguerreotype	Light	Destroyed		2
Iodine	G. Wardley	1862	Daguerreotype	Light	Destroyed		3
Iodine, in alcohol	W. de W. Abney	1877	Collodio-bromide emulsion	Light	Destroyed		6
Iodine	J. M. Eder	1895	Collodio-bromide emulsion	Light	Destroyed		14
Iodine	J. M. Eder	1895	Collodio-bromide emulsion	Emulsion	Destroyed (after 12 hours)		17
Iodine	J. Milbauer and J. Flek	1924	High-speed gelatin emulsion	Storage	Reduced	(Gradation unaltered)	89
Iodine oxyacids	J. M. Eder	1895	Collodion emulsion	Emulsion or storage	Destroyed		16

Summary—continued

Chemical Agent(s) (in solution in water)	Authority	Year	Material or Process	Means of for- mation of latent image (or fog)	Effect of bath on latent image (or fog)	Effect of bath on sensitivity to light	Reference Number
Mercuric chloride	J. M. Eder	1903	Collodion or gelatin emulsion	Light	Destroyed		12
Mercuric chloride	R. A. Reiss	1901	Gelatino-bromide emulsion	Light	Destroyed	Reduced	29
Mercuric chloride	J. M. Eder	1903	Gelatino-bromide emulsion	Light	Destroyed		40
Mercuric chloride	A. Steigmann	1921	Gelatin emulsion	Light	Progressive weakening and eventual destruction		70
Mercuric chloride	A. Steigmann	1922	Low-speed gelatin emulsion	Light	Great weakening for post-fixation mercury or silver development	Very greatly reduced if treatment is not followed by washing	74
Mercuric nitrate	J. M. Eder	1895	Wet collodion, and silver iodide on glass	Light	Destroyed		4
Mercuric nitrate	J. M. Eder	1895	Wet collodion	Light	Survives treatment sufficient to remove developed silver image		4
Mercuric nitrate	J. M. Eder	1906	Collodio-chloride plates	Light	Destroyed		48
Mercuric nitrate	A. Steigmann	1922	Low-speed gelatin emulsion	Light	Destroyed for post-fixation physical development		74
Mercuric salts	S. E. Sheppard and C. E. K. Mees	1907	Gelatin emulsion			Diminished	50
Mercuric salts	G. Kögel and A. Steigmann	1925	Gelatin emulsion			Tremendously reduced, when treatment not followed by washing	104
Mercuric thiocyanate complex salt	A. Steigmann	1921	Gelatin plates	Light	Progressive weakening and eventual destruction		70
Metal "perchlorides"	J. M. Eder	1903	Gelatino-bromide emulsion	Emulsion or storage, and light	Tendency to, or actual, destruction, when subjected to emulsion in preparation	Lowered	43

Summary—continued

Chemical Agent(s) (in solution in water)	Authority	Year	Material or Process	Means of formation of latent image (or fog)	Effect of bath on latent image (or fog)	Effect of bath on sensitivity to light	Reference Number
Metal "perchlorides"	J. M. Eder	1906	Collodiochloride plates	Light	Destroyed		48
Nitric acid, with hydrochloric acid	J. M. Eder	1906	Collodiochloride plates	Light	Destroyed		48
Nitrous acid	J. M. Eder	1895	Collodiochloride emulsion	Light	Destroyed		15
Nitrous acid	J. M. Eder	1903	Gelatino-bromide emulsion	Light	Destroyed		40
Nitrous acid	A. Rossi	1925	Gelatin emulsion plates	Light	A certain amount of reduction may occur		103
Potassium chlorate, with hydrochloric acid	J. M. Eder	1903	Gelatino-bromide emulsions	Emulsion or storage, and light	Tendency to, or actual, destruction, when added to emulsion in preparation	Lowered	43
Potassium chromate, with $\text{Cr}_2(\text{SO}_4)_3$, KCl and HCl	R. Luther	1899	Silver chloride on glass	Light	Destroyed by a solution of oxidation potential 1.45 v.; only slightly reduced by one of 1.35 v.		22
Potassium chromate with $\text{Cr}_2(\text{SO}_4)_3$, KBr and H_2SO_4	R. Luther	1899	Silver chloride on glass	Light	Destroyed by a solution of oxidation potential 1.19 v.; not destroyed by one of 1.09 v.		22
Potassium dichromate	W. de W. Abney	1877	Collodio-bromide	Light	Not destroyed		8
Potassium dichromate	W. de W. Abney	1877	Collodio-iodide	Light	Destroyed		8
Potassium dichromate	W. de W. Abney	1881	Wet collodio-iodide	White light	Destruction accelerated by exposure to red light after treatment not followed by washing		9
Potassium dichromate	W. de W. Abney	1881	Gelatino-bromide plate	White light	Destruction accelerated by exposure to red light after treatment not followed by washing		9

Summary—continued

Chemical Agent(s) (in solution in water)	Authority	Year	Material or Process	Means of formation of latent image (or fog)	Effect of bath on latent image (or fog)	Effect of bath on sensitivity to light	Reference Number
Potassium dichromate	W. B. Bolton	1884	Gelatin emulsion	Light	Only slightly reduced as regards number of exposure fields; greatly reduced, however, as regards contrast		10
Potassium dichromate	W. de W. Abney	1885	Gelatin emulsion	Emul- sion	Destroyed	Slightly reduced	11
Potassium dichromate	J. M. Eder	1895	Collodion emulsion	Emul- sion	Destroyed		16
Potassium dichromate	L. Vidal	1903	Gelatin emulsion	Storage	Destroyed		38
Potassium dichromate	L. Vidal	1903	Gelatin emulsion	Light	Unaffected		38
Potassium dichromate	J. M. Eder	1903	Gelatino- bromide	Emul- sion or storage, and light	Destroyed		41
Potassium dichromate	J. M. Eder	1903	Gelatino- bromide emulsion	Emul- sion or storage, and light	Tendency to, or actual, de- struction, when added to emulsion in prepara- tion	Lowered	43
Potassium dichromate	J. Sterry	1904	Low-speed gelatino- chloride and bromide emulsions	Light	Not destroyed as regards number of exposure fields; but densities reduced and curve so modified that great contrasts are correctly rendered		45
Potassium dichromate	J. Waterhouse	1904	Gelatin emulsion	Light	Not readily destroyed		46
Potassium dichromate	J. Sterry	1907	Low-speed gelatino- chloride and bromide emulsions	Light	Not de- stroyed; but image may develop more slowly. (In part changed into a less, or non-, devel- opable con- dition)		53

Summary—continued

Chemical Agent(s) (in solution in water)	Authority	Year	Material or Process	Means of formation of latent image (or fog)	Effect of bath on latent image (or fog)	Effect of bath on sensitivity to light	Reference Number
Potassium dichromate	R. B. Wilsey	1917	Low-speed gelatin emulsions	Light	Not destroyed; but contrast largely reduced and scale increased		63
Potassium dichromate	Lüppo-Cramer	1924	Gelatin "lantern" plates	Light	Bath of NaOH either before exposure or between exposure and $K_2Cr_2O_7$ treatment hastens or increases the latent image destroying action of the latter		90
Potassium dichromate	Lüppo-Cramer	1925	Gelatin emulsion ripened by boiling	Light	More extensively destroyed if preceded by NaOH solution		100
Potassium dichromate, with acid	A. Lumière, L. Lumière, and A. Seyewetz	1911	Gelatin emulsion	Light	Partially destroyed by treatment sufficient to remove developed silver image		57
Potassium dichromate, with hydrochloric acid	J. M. Eder	1895	Collodion emulsion	Emulsion	Destroyed		16
Potassium dichromate, with hydrochloric acid	J. M. Eder	1903	Gelatino-bromide emulsion	Emulsion or storage, and light	Destroyed		41
Potassium dichromate, with mineral acid	J. M. Eder	1903	Gelatino-bromide emulsion	Emulsion or storage, and light	Tendency to, or actual, destruction, when added to emulsion in preparation	Lowered	43
Potassium dichromate, with nitric acid	J. M. Eder	1902	Gelatino-bromide emulsion	Light	Destroyed: latent image of <i>solarizing</i> exposures converted into one that develops normally		33
Potassium dichromate, with nitric acid	J. M. Eder	1903	Gelatino-bromide emulsion	Emulsion or storage, and light	Destroyed		41

Summary—continued

Chemical Agent(s) (in solution in water)	Authority	Year	Material or Process	Means of formation of latent image (or fog)	Effect of bath on latent image or (fog)	Effect of bath on sensitivity to light	Reference Number
Potassium dichromate, with nitric acid	J. Waterhouse	1904	Gelatin emulsion	Light	Destroyed		46
Potassium dichromate, with nitric acid	Lüppo-Cramer	1905		Light	Destroyed: latent image of <i>solarizing</i> exposures converted into one that develops normally		47
Potassium dichromate, with nitric acid	G. Chierchia	1922	Gelatin emulsion	Light or storage	Destroyed	Reduced somewhat	73
Potassium dichromate, with nitric acid	L. J. G. van Ewijk and H. J. Prins	1925	Gelatin emulsion	Light	Unaffected for chemical (glycin) development, by treatment sufficient to remove developed silver image		103
Potassium dichromate, with sulfuric acid	W. B. Bolton	1884	Gelatin emulsion	Light	Destroyed		10
Potassium dichromate, with sulfuric acid	J. M. Eder	1903	Collodion or gelatin emulsion	Light	Destroyed		12
Potassium dichromate, with sulfuric acid	Lüppo-Cramer	1901	Collodion emulsion	Light	Destroyed	Reduced to about 1/5th	25
Potassium dichromate, with sulfuric acid	J. M. Eder	1902	Gelatino-bromide emulsion	Light	Destroyed: latent image of <i>solarizing</i> exposures converted into one that develops normally		33
Potassium dichromate, with sulfuric acid	J. M. Eder	1903	Gelatino-bromide emulsion	Emulsion or storage, and light	Destroyed		41
Potassium dichromate, with sulfuric acid	H. Engelken	1924	Gelatin emulsion	Storage	Destroyed	Reduced to about 1/3rd if treatment is followed by bathing in rodinal and then alcohol	88

Summary—continued

Chemical Agent(s) (in solution in water)	Authority	Year	Material or Process	Means of formation of latent image (or fog)	Effect of bath on latent image (or fog)	Effect of bath on sensitivity to light	Reference Number
Potassium dichromate, with sulfuric acid and potassium bromide	G. Chierchia	1922	Gelatin emulsion	Light	Destroyed, simultaneously with the bleaching of a developed silver image		73
Potassium dichromate, with sulfuric acid	H. Arens	1925	Gelatin emulsion	Light	Destroyed: Eder's observation (ref. 33) regarding action on solarizing exposures confirmed		97
Potassium ferric oxalate	J. M. Eder	1903	Gelatino-bromide emulsion	Light	Destroyed		40
Potassium ferric oxalate	Lüppo-Cramer	1922	Certain gelatin emulsions		Fog <i>produced</i> by bathing in freshly prepared dilute solution, and drying	Diminished greatly	75
Potassium ferricyanide	Lüppo-Cramer	1901	Collodion emulsion	Light	Impaired	Somewhat impaired	25
Potassium ferricyanide	J. M. Eder	1903	Gelatino-bromide emulsion	Light	Destroyed		40
Potassium ferricyanide	J. M. Eder	1903	Gelatino-bromide emulsion	Emulsion or storage, and light	Tendency to, or actual, destruction, when added to emulsion in preparation	Lowered	43
Potassium ferricyanide	J. M. Eder	1906	Collodio-chloride plates	Light	Destroyed		48
Potassium ferricyanide	E. Demole	1907	Gelatin emulsion	Light	Not destroyed as regards number of exposure fields; but densities are reduced		54
Potassium ferricyanide	A. Steigmann	1922	Low-speed gelatin emulsion	Light	Not destroyed, but densities reduced; action accelerated by addition of potassium bromide		74

Summary—continued

Chemical Agent (s) (in solution in water)	Authority	Year	Material or Process	Means of formation of latent image (or fog)	Effect of bath on latent image (or fog)	Effect of bath on sensitivity to light	Reference Number
Potassium ferricyanide	Lüppo-Cramer	1907	Gelatin emulsion	Light vs. emulsion or storage	The light-image is destroyed before the fog. With certain concentrations, fog is increased		59
Potassium ferricyanide, with potassium bromide	A. Steigmann	1922	Low-speed gelatin emulsion	Light	Not destroyed for chemical development; completely destroyed for physical development if treatment is followed by fixing in thiosulfate		74
Potassium ferricyanide, with sodium thiosulfate	Lüppo-Cramer	1901	Collodion emulsion plates	Light	Easily destroyed for physical development		26
Potassium ferricyanide, with sodium thiosulfate	A. Steigmann	1922	Low-speed gelatin emulsion	Light	Destroyed for physical development		74
Potassium permanganate	W. de W. Abney	1877	Collodio-bromide	Light	Slowly destroyed		8
Potassium permanganate	W. de W. Abney	1877	Collodio-iodide	Light	Destroyed		8
Potassium permanganate	W. de W. Abney	1877	Wet collodio-iodide	White light	Destruction accelerated by exposure to red light after treatment not followed by washing		9
Potassium permanganate	Lüppo-Cramer	1901	Collodion emulsion	Light	Almost completely destroyed	Very greatly reduced	25
Potassium permanganate	J. Sterry	1907	Gelatin emulsion	Light	In part changed into a less, or non-, developable condition		53

Summary—continued

Chemical Agent(s) (in solution in water)	Authority	Year	Material or Process	Means of formation of latent image (or fog)	Effect of bath on latent image (or fog)	Effect of bath on sensitivity to light	Reference Number
Potassium permanganate	Lüppo-Cramer	1907	Gelatin emulsion	Light vs. emulsion or storage	The light-image is destroyed before the fog. With certain concentrations fog is increased		59
Potassium permanganate	G. A. Perley	1909 1910	Low-speed gelatin emulsion			Tendency towards solarization checked	60 61
Potassium permanganate, with sulfuric acid	R. Namias	1901	Medium-speed gelatin emulsion	Light	Destroyed	Almost completely removed	28
Potassium permanganate, with sulfuric acid	A. Lumière, L. Lumière, and A. Seyewetz	1911	Gelatin emulsion	Light	Unaffected, for post fixation physical development, by treatment sufficient to remove developed silver image		57
Potassium persulfate	Lüppo-Cramer	1907	High-speed gelatin emulsion	Light	While diminishing the light-image, fogs the plate completely		59
Potassium persulfate	J. Milbauer and J. Flek	1924	Gelatin emulsion	Storage	Destroyed by heating to 100°C. for 10 min. and then in persulfate solution	Reduced to about 1/9th	89
Selenium	<i>J. Soc. Chem. Ind.</i>	1922	Gelatin emulsions		(Tendency to fog in development is not increased)	Reduced, when added to emulsion in preparation	68
Sodium thiosulfate, with sulfuric acid	F. Kogelmann	1895	Gelatino-bromide emulsion plates	Light	Destroyed: latent image of solarizing exposures converted into one that develops normally		18

Summary—continued

Chemical Agent(s) (in solution in water)	Authority	Year	Material or Process	Means of formation of latent image (or fog)	Effect of bath on latent image (or fog)	Effect of bath on sensitivity to light	Reference Number
Sulfur	<i>J. Soc. Chem. Ind.</i>	1922	Gelatin emulsions		(Tendency to fog in development is not increased)	Reduced, when added to emulsion in preparation	68
Tellurium	<i>J. Soc. Chem. Ind.</i>	1922	Gelatin emulsions		(Tendency to fog in development is not increased)	Reduced, when added to emulsion in preparation	68
"Tincture of bromine"	J. M. Eder	1895	Collodion emulsion	Emulsion	Destroyed, when added to emulsion in preparation	Destroyed, when added in too large quantity, to emulsion in preparation	16
"Tincture of bromine"	J. M. Eder	1903	Gelatino-bromide emulsion	Light	Destroyed		40
Tincture of iodine	G. Shadbolt	1861	Wet collodion, and albuminized collodion	Light	Destroyed		1
Tincture of iodine	J. M. Eder	1895	Collodion emulsion	Emulsion	Destroyed, when added to emulsion in preparation	Destroyed, when added in too large quantity, to emulsion in preparation	16
Tincture of iodine	J. M. Eder	1903	Gelatino-bromide emulsion	Light	Destroyed		40
Tincture of iodine	J. M. Eder	1903	Gelatino-bromide emulsion	Emulsion or storage, and light	Destroyed		41

In the case of high-speed gelatin emulsions the distribution of the latent image in the depth of the silver halide grain assumes importance, and, as discussed in the next chapter, it is somewhat difficult to judge destruction of latent image by a given solution. Differences in the criteria adopted account, doubtless, for the notable differences recorded in the action of solutions of relatively low oxidation potential, such as unacidified dichromate, on the latent image. The evidence presented in this review of the literature is not sufficiently consistent to allow any suggestion as to the possible identity of latent chemical fogs with the latent light-image.

Silver-Oxidizing Baths, Their Division into Two Classes According to Whether Their Action on the Latent Image is Predominantly an Increase in Inertia or a Decrease in Gamma, the Reason for This Difference, and a Tentative Criterion of Destruction of the Latent Image

The latent image is generally held to consist of elementary silver formed by the action of light. It is also possible that elementary silver plays a part in the sensitivity of ripened emulsions, being formed during the emulsion process. It is therefore of interest to observe any correlation between the capacity of a given solution to oxidize silver and its destroying action on the latent image or on high-speed sensitivity.

The general plan in these experiments was to impress a standard light exposure on one-half of an emulsion film, to submit the film to the action of the particular solution for the desired time, to treat the film by a process that would remove the excess of the solution and its reaction products with the gelatin, without itself appreciably affecting the latent image and sensitivity, to impress the standard light exposure on the unexposed half of the film, and finally, to develop the whole film under standard conditions.

The procedure in the case of acidified permanganate and Eastman Commercial film is as follows: One-half of a 6.5 by 4.25 inch sheet of the film was exposed behind a Chapman-Jones plate tester, the other half being protected from light. The source of light was a 25-watt Mazda filament lamp which was run at its rated voltage, and the exposure such that on development approximately the first eighteen of the neutral tint squares became visible. The bath was potassium permanganate (0.2 per cent) containing sulfuric acid (1 per cent). The film was immersed in this, at 20° C., and kept in motion for the desired time, usually 1 to 30 minutes; then transferred to running city water and kept in motion for about one minute; again transferred to a clearing solution of sodium bisulfite (5 per cent) with sulfuric acid (0.5 per cent) and kept in motion for about 10 minutes; rinsed in running city water; and left to soak with occasional handling, in a solution of potassium bicarbonate (0.2 per cent) with potassium bromide (0.0025 per cent) for one hour. The adhering solution was removed from

the film by shaking or mopping, and the film hung in the darkroom to dry. The darkroom was ventilated by the washed air supply of the laboratory, and its temperature during the winter months was maintained close to 20°C . When dry, the half of the film not previously exposed, was now exposed under the same conditions as the first, and the whole film was developed in a particular elon-hydroquinone developer for 2.5 minutes at 20°C ., which gives a gamma of about 1.3 for untreated film, fixed in an acid-hardening fixing bath, washed, and dried. This permanganate after-treatment had previously been proved to have no very appreciable effect on Eastman Commercial film as regards either fog or general or spectral sensitivity, yet it is very effective in removing both oxidizer and acid from the emulsion film.

Three different permanganate baths were used,—an acid bath of potassium permanganate with sulfuric acid, a bath of permanganate alone, and an alkaline bath of permanganate with sodium carbonate. The acid bath causes a reduction in sensitivity, destruction of the latent image, and no fog; the plain and alkaline baths leave sensitivity unaffected, cause a lowering of gamma, a doubtful complete loss of the latent image corresponding to the feeblest exposures, and again no fog. Potassium permanganate with *nitric* acid causes reduction in sensitivity, destruction of the latent image and no fog; and the same qualitative results are given by ammonium persulfate with sulfuric acid, sodium nitrite with sulfuric acid, chromic acid with sulfuric acid, and chromic acid alone. At similar concentrations, the acid permanganate baths are usually the quickest in action. In the case of sodium nitrite with sulfuric acid, complete destruction of the latent image is observed only after repeated application of freshly mixed bath.

The fraction of original sensitivity remaining after treatment with acid permanganate is smaller than with acid persulfate. In each case, sensitivity appears to decrease continuously during the period required for the destruction of the latent image imposed by the standard first exposure. Successive baths of permanganate alone or with alkali, and sulfuric acid, have the same effect as the single bath of acid permanganate, namely, pronounced lowering of sensitivity and destruction of latent image. Hydrogen peroxide with sulfuric acid appears to lower sensitivity, to destroy latent image, and to produce fog. Potassium iodate with sulfuric acid, and also potassium bromate with sulfuric acid, act in the same manner as acid permanganate, lowering sensitivity and destroying latent image without creating fog. Potassium chlorate with

sulfuric acid destroys the latent image only very slowly, in apparent harmony with the slowness of its "bleaching" action as compared with acidified bromate or iodate, on a developed silver image. Potassium ferricyanide in solution, alone or with soluble bromide or chloride, gives little or no loss of sensitivity, but lowers the contrast (gamma) of the latent image considerably, and in each case to the same extent. The baths used were potassium ferricyanide (1 to 5 per cent), potassium ferricyanide (1 per cent) with potassium bromide (1 per cent), and potassium ferricyanide (1 per cent) with sodium chloride (1 per cent), for twenty minutes, followed by ten minutes' washing in running water. An old experiment was repeated in which a silver image was immersed in a ferricyanide-bromide solution and left in the dark as long as the gelatin would remain on the support. Then the "bleached" image was immediately developable without exposure to light. This developability is, however, wholly removed if a bath of dilute dichromate or very dilute acid permanganate be interposed before attempted development.

Four halidizing baths were tried,—chromic acid with potassium bromide, potassium permanganate with potassium bromide, mercuric bromide, and mercuric chloride. In every case there was lowering of sensitivity and destruction of latent image, without creation of latent fog. Mercuric salts, if completely removed, do not cause an extreme lowering of sensitivity; when the standard latent image is just destroyed, the sensitivity in the case of Eastman Commercial film is of the order of one-fourth of the original. Preliminary experiments with cupric bromide and ferric bromide show results similar to those with mercuric salts. Alternate baths of dilute hydrochloric acid and water were used to remove the excess of the metallic salt.

When Eastman Commercial Ortho film is treated in a solution of potassium permanganate with potassium bromide, followed by bisulfite, *etc.*, the blue sensitivity is slightly lowered while the dye-imparted color-sensitivity is destroyed. Serious fog resulted, while with regular Commercial film in the same baths no fog is found.

In the foregoing experiments the extent of loss of latent image was, as indicated in the general description, judged by comparison of an exposed-treated-developed film with one that had been treated-exposed-developed. It was observed that a loss of latent image as thus determined was invariably accompanied by lowering of sensitivity.

Subsequent experiments made at intervals during 1919 to

1924, and prior to the commencement of the systematic investigation into the apparently anomalous action of potassium ferricyanide solution on the latent image and sensitivity, are recorded in the following pages.

Treatment with acid permanganate, followed by bisulfite, entirely destroys the latent edge-fog of old (stored) panchromatic plates.

It was observed that deposition of sulfur in an unexposed Eastman Commercial film by alternate baths of dilute sulfuric acid and dilute hypo fails to produce latent fog. When sodium selenosulfate is used instead of hypo, red stain and latent fog result. It was found that if a very little acid permanganate is added to a potassium ferricyanide solution the bath will not destroy a latent image, but if the permanganate content is increased, and the bath followed by bisulfite, the latent image is destroyed and sensitivity greatly diminished.

Earlier experiments on the action of potassium ferricyanide solution on the latent image were extended by acidifying the bath with varying contents of sulfuric acid, and by using yellow-dyed emulsions, with, or without blue light-filters. The results showed only a great reduction in gamma, with no quite undoubted destruction of latent image in any case.

Experiments on the action of potassium permanganate with potassium bromide on the latent image do not always show complete destruction, and it is surmised that the conjoint action of atmospheric carbon dioxide or free acidity in the emulsion may be essential for the effect. In other words, it seems possible that in the absence of acid, potassium permanganate with potassium bromide may act in the same way as permanganate alone, though more quickly.

To test the suggestions (1) that the true latent image destroying agent in the case of the application of a silver solvent bath may be bromine which is set free by the action of the oxidizing agent on traces of soluble bromide normally present in a bromo-iodide emulsion, and (2) that the action of a silver solvent on the latent image brings about a local depression of sensitivity greater than the general depression, the following series of experiments was carried out. All apparently unessential conditions were changed as far as possible, to eliminate any specific effects and to find whether or not it is generally true that a solvent of silver is a destroyer of the latent image. Four emulsions were used, namely, Eastman Commercial film, pure silver bromide emulsion plates, Seed Non-Halation Ortho plates, and Wratten and Wainwright Panchromatic plates. Using similar methods of after-treatment for removal of the

oxidizing substances, the earlier results were first without exception qualitatively confirmed. After the first impressed exposure, these four emulsions were next bathed in 0.1 per cent silver nitrate solution for 15 minutes at 20° C., and then rinsed in distilled water prior to immersion in the silver solvent bath which was carefully kept free from soluble halides, and subsequently washed in changes of 0.001 per cent silver nitrate solution, allowed to dry, and given the second exposure. For the permanganate baths it was necessary to reduce the potassium permanganate concentration to 0.005 per cent, keeping the acid concentration at one per cent and to maintain the potassium permanganate concentration by adding further permanganate (in the form of more concentrated solution) equivalent to 0.001 per cent of the bath, every two minutes; under these conditions the latent image is destroyed in 10 to 20 minutes and the emulsion film is not visibly discolored nor rendered unduly insensitive. The second exposure was made on the same portion of film, but a simple exposure tablet of ten density bands was used and this was so arranged that the second exposure crossed the first at right angles. The second exposure was ten times the first. Both exposures were made through a blue filter. Preliminary experiments had shown that silver nitrate treatment, with suitable restrictions of concentration, time of action, and time elapsing before giving the second exposure and development, does not give appreciable fog, yet is effective in removing the soluble bromide normally present in an emulsion film. The results, as regards the destruction of the latent image, were entirely concordant and confirmatory of former results. In no case of complete destruction of the latent image could an indication be traced of any variation in sensitivity for the second exposure due to the impression and destruction of the first latent image. (In the greater number of those cases in which, owing to inadequacy of time of action of the oxidizing bath, the first latent image had not been destroyed, the effect of the two light impressions was additive; a certain degree of antagonism was observed in other cases.) The results of these later experiments lend, therefore, support to the thesis that a solvent of silver is a destroyer of the latent image.

Emulsions, bathed in bromine water and dried, were exposed intensely to give print-out images; the effect of a developer on these resembles proportional intensification, with no suggestion of light-reversal. Light-reversing, so-called solarizing, exposures, after treatment with acid permanganate and then bisulfite, leave a diminished print-out image which acts

in a developer somewhat like the bromine-treated and printed-out emulsions. The developed image is in direct sequence.

The print-out densities of light reversing and re-reversing exposures, which are removed slowly by the action of acid permanganate applied directly, are removed almost instantly if fixing has intervened.

Many experiments were made on the action of silver oxidizing baths with physical instead of chemical development. For pre-fixation physical development, results were broadly identical with those for chemical development. For post-fixation development, however, parallelism obtains only under certain conditions, and some new and interesting facts appear. The latent image of relatively low light exposures is irrecoverably removed by baths of three classes: (1) Silver solvent, capable of converting silver into a simple salt (such baths are acid permanganate and acid persulfate); (2) silver solvent, capable of converting silver into a complex salt (such baths are aerated hypo and Farmer's reducer); (3) sulfidizing baths (such as polysulfide and hypo-alum). The action of bromidizing or iodidizing baths, such as ferricyanide-bromide or ferricyanide-iodide, harmonizes with the view that after fixation the latent image is silver. In a bath such as dilute ferricyanide-bromide the latent image is rapidly destroyed as such, but with suitable treatment it may be largely regained by a flash exposure. There is a strong suggestion that what is taking place in the operation is a transformation to silver bromide or iodide, a partial dissolution of this in the bath and washing water, and retransformation of what remains in the film to silver. An emulsion treated with acid permanganate followed by bisulfite fogs less rapidly on prolonged immersion in either a chemical or a physical developer than does the untreated emulsion. An emulsion thus treated does not show diminution in opacity for actinic light.

Compared with cupric bromide or chloride, copper sulfate solution, without added soluble bromide, shows only a feeble action on the latent image and sensitivity: this is in harmony with the relative rates of reaction of the solutions with silver.

Consideration of the literature which is reviewed in Chapter I in conjunction with the writer's independent experiments which have been described, leads to a recognition of two classes of silver-oxidizing solutions.

The greater number of substances which in aqueous solution are capable of converting silver into a salt or salts of silver, so act on the latent image that, after removal of the excess agent and any reaction product with the gelatin, and developing,

the lowest exposures are apparently lost, the density ("characteristic") curve is displaced in the direction of increased $\log E$, and the sensitivity of unexposed portions of the emulsion film is invariably lowered. A minority of silver oxidizers act differently. These reduce the steepness of the characteristic curve without clearly removing the latent image of even the lowest exposures. The latter effect, which is enormous under certain conditions, is not accompanied by any lowering of sensitivity. This difference is well-marked and calls for an inquiry into its significance.

In the first class we find, for example, cupric bromide, iodic acid, and potassium permanganate with sulfuric or nitric acid: these are substances whose potential for a reaction with silver is obviously high; the second class consists of potassium dichromate without added acid, potassium ferricyanide, and potassium permanganate without acid or with alkali, substances whose potential for a reaction with silver is relatively low.

The latter class is now considered in detail. Bolton¹ records that a solution of potassium dichromate applied after exposure behind a tablet, only slightly reduces the number of fields developable, but greatly reduces contrast. Demole² describes a similar effect with potassium ferricyanide solution. The writer observed that potassium permanganate solution, alone or with sodium carbonate, reduces the gamma of the image without undoubtedly removing the lowest exposures and without lowering sensitivity.

Of these three substances, potassium ferricyanide, because of the apparent simplicity of its reaction with silver, because this reaction is not affected by small variations in acidity or alkalinity, and because it does not, as far as is known, yield products that harden gelatin, was chosen for new experiments.

The reaction between potassium ferricyanide solution and silver was investigated by Eder.³ Allowing for incompleteness under the conditions of the experiment—about 3 - 4 per cent of the silver remained untransformed—the results indicated that the reaction occurred in accordance with the equation:



Whether this reaction would be strictly quantitative as regards the conversion of silver by means of an excess of potas-

¹ W. B. Bolton: Potassium Bichromate and the Undeveloped Image. *Brit. J. Phot.* **31**: 49. 1884 (Jan. 25).

² E. Demole: Contribution à l'étude de l'image latente photographique. *Comp. rend.* **144**: 565. 1907 (March 11).

³ J. M. Eder: Ueber die Einwirkung von Ferridcyaniden auf metallisches Silber. *J. prakt. Chem.* (2) **16**: 211. 1877 (Aug. 11).

sium ferricyanide in solution to silver ferrocyanide under conditions of adequate time and facility of access of the solution to the silver element, is not quite certain. If the reaction products are exclusively those given in the equation, namely, potassium ferrocyanide and silver ferrocyanide, then 96 per cent of the silver being transformable, no reason can be assigned why, with excess of potassium ferricyanide, in this heterogeneous system, the remaining 4 per cent should not be likewise transformable. When pure precipitated silver is agitated with an excess of potassium ferricyanide in concentrated aqueous solution, and the solid product washed, then extracted with an excess of sodium sulfite in concentrated aqueous solution, and the residue again washed, it is seen under a microscope by reflected light, that the solid product consists of lumps having a smooth, grayish surface while the residue after sulfite extraction has the appearance of the original precipitated silver. The operations of treating with ferricyanide, and then with sulfite, may be repeated a number of times if the original silver is somewhat coarse; the appearances under the microscope after ferricyanide treatment are always similar, and the residue after sulfite always resembles metallic silver. When a dilute ferricyanide solution is added to a turbid, red colloidal solution of silver, there is no immediate change in appearance, but a gradual bleaching sets in and may continue during several minutes. These observations favor the suggestion that the apparent incompleteness of conversion of silver to silver ferrocyanide by excess of potassium ferricyanide in solution is wholly due to the difficulty which the ferricyanide ion experiences in penetrating the film of silver ferrocyanide that covers the residual silver. There does not appear to be any evidence in the literature to support a suggestion of a solid reaction product other than silver ferrocyanide. It is concluded, therefore, that in the absence of knowledge to the contrary, Eder's equation expresses the reaction.

The accompanying figure illustrates the action of ferricyanide on the latent image of a high-speed emulsion (Eastman Super-Speed Portrait film). Each of the curves shown is formed by splicing, or attempting to splice, density curves for two exposure ($\log E$) scales, the exposure times of which differ by a factor of 128. If the reciprocity law holds, they will overlap for a certain distance, since the intensity scale in each case is considerably greater than 1 : 128. The exposure was to blue light. For the control (the exposed emulsion that was bathed in distilled water for the same time as the experimental piece

was bathed in ferricyanide, washed in a similar manner, and developed), the overlap is practically perfect, while for the emulsion that was bathed in 0.5 per cent potassium ferricyanide solution for 10 minutes and washed in running city water for 40 minutes, between exposure and development, the two parts do not overlap at all. A further effect is the removal of the initial stage of solarization. For convenience of illustration the ordinates of the lower curves are approximately doubled.

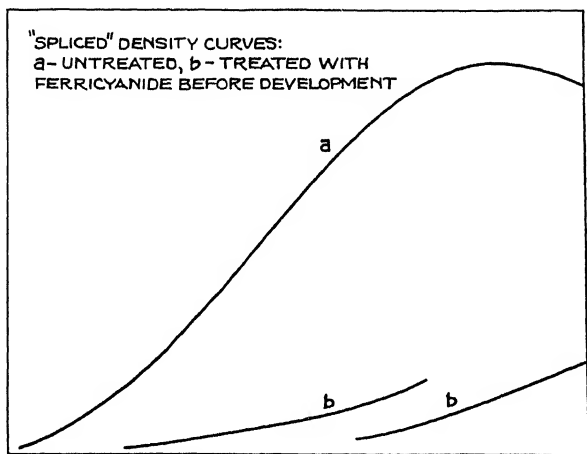


FIG. 1

Development was in an elon-hydroquinone developer for a moderate time. It seems not impossible that continued development of the ferricyanide-treated emulsion might diminish, or even obliterate, the gap between the two portions. The result for moderate development, however, indicates that the susceptibility of a low-intensity and high-time exposure to the action of ferricyanide is greater than that of a high-intensity and proportionately lower time exposure.

The suggestion of a close relation between ferricyanide action and depth distribution of the latent image in the grain led to experiments in which a constant ferricyanide treatment and washing were given but the kind of development varied. An endeavor was made to obtain a gamma of about 2 for the untreated emulsion film. For the gamma of the treated film, the mean slope of the (single-time intensity scale) density curve was taken over the exposure range corresponding to the

straight-line portion of the untreated film. The results for two different emulsions are tabulated below:

Development	<i>Eastman Slow Lantern Plate</i>		<i>Eastman Commercial Film</i>	
	Gamma		Gamma	
	H ₂ O-treated	K ₃ Fe(CN) ₆ -treated	H ₂ O-treated	K ₃ Fe(CN) ₆ -treated
In elon-hydroquinone	2.00	0.07	1.82	0.10
In ferrous oxalate	2.15	.03	1.92	.003
Pre-fixation physical	2.11	.04	1.78	.036
Post-fixation physical	1.70	.42	1.70	.94

Taking the two emulsions together, it is seen that for post-fixation physical development the ferricyanide treatment after exposure has reduced the gamma to about 2/5ths, for alkaline development to about 1/22nd, for pre-fixation physical development to about 1/51st, and for ferrous oxalate development to about 1/123rd. These figures are but arbitrary measures of the ferricyanide gamma-reducing effect, since the density curves of untreated and treated sensitive material do not strictly correspond. The physical developer used was elon, 2; citric acid, 10; water, to each 100 c.c.; with 3 c.c. of 10 per cent silver nitrate solution added immediately before use; development being at 18° C. The fixing bath was ordinary acid-hardening hypo *after development*, and 18 per cent pure anhydrous sodium sulfite solution *before development*.

The difference in the figures suggests that while the ferricyanide solution acts only on the latent image nuclei in the surface of the silver halide grain, development is affected by nuclei beneath the surface. Before attempting to check the value of this suggestion by further experiment it was desirable to find the effect of varying the concentration and time of action of the ferricyanide and the time of washing.

Using Eastman Commercial film, concentrations of potassium ferricyanide of 0, 0.05 per cent, 0.5 per cent, and 5 per cent gave gammas of 1.73, 0.17, 0.12, and 0.11, respectively. A later test, for concentrations of 0.001 per cent, 0.005 per cent, 0.015 per cent, and 0.05 per cent, gave respective gammas of 0.72, 0.14, 0.13, and 0.14. The time of immersion in each case was 10 minutes. It may be concluded that a ferricyanide concentration as low as 0.005 per cent produces an effect approximately equal to that produced by a 5 per cent solution. With a 0.001 per cent solution, in the given time, there is a decided falling off.

The time of immersion in a 0.5 per cent ferricyanide solution was varied. Using Eastman Commercial film, times of 0, 2, 10, and 40 minutes gave gammas of 1.71, 0.09, 0.11, and 0.17. This increase of gamma on prolonging immersion being unexpected, a repetition was made of the 2 and 40 minutes' immersion: the result was now 0.10 and 0.11, respectively. Using Slow Lantern plates, immersions of 0, 2, 10, and 40 minutes gave gammas of 2.13, 0.06, 0.09, and 0.10, respectively. These figures suggest a tendency for the gamma to rise on continued immersion. It is clear, however, that an immersion of 2 minutes (possibly much less) suffices to bring about a great lowering of gamma.

Since potassium ferrocyanide is a product of the reaction between potassium ferricyanide and silver, a test was made in which the former was used instead of the latter. Eastman Commercial film was exposed, bathed in 0.5 per cent potassium ferrocyanide solution for ten minutes, washed forty minutes, and developed in an elon-hydroquinone developer, as before. Compared with the blank test in which distilled water was used, the result was slightly greater fog, a somewhat lower gamma, and doubtful loss of latent image (that is, doubtful removal of the lowest exposure field).

It seems probable that potassium ferrocyanide produces these effects in consequence of its slight action on silver bromide, producing a little silver ferrocyanide, the molar solubility of which, though somewhat, is not very much greater, than that of silver bromide, and that there is no connection between these effects and the very conspicuous gamma-reducing (and non-fogging) action of ferricyanide.

The effect of varying the duration of washing between ferricyanide-bathing and development was tested: 0, 5, 25, and 125 minutes' washing gave gammas of respectively 0.07, 0.07, 0.05, and 0.11.

The effect of varying the concentration of the developer was tested by comparing the gammas obtained in the usual time (3 minutes) and at the usual temperature (20° C.) when the elon-hydroquinone developer was used (i) undiluted, (ii) diluted to one-half, and (iii) diluted to one-quarter concentration. The results are:

<i>Concentration of Developer</i>	<i>Gamma of Untreated Film</i>	<i>Gamma of Treated Film</i>	<i>Ratio</i>
1	1.75	0.08	1/22
½	1.46	.032	1/46
¼	1.18	.016	1/74

It seems clear that the gamma-lowering effect of ferricyanide increases with dilution of the developer, probably owing to decreasing silver halide solvent action due to decreasing sulfite content.

The light by which the standard exposures were made in the above-described experiments was that of a 250-watt metal filament lamp run at less than the rated voltage, passed through a blue filter, the latter being used for convenience in prolonging the exposure time and also in order that the exposing light should be spectrally somewhat more definite. The emulsions used being non-color-sensitive, it was not expected that the use of blue as compared with white light would affect the results sought. A comparison was made, however, using the lamp at its rated voltage, omitting the blue filter and suitably increasing the distance of the sensitive material: little or no difference was observed.

It has been seen that, after ferricyanide treatment, the gammas obtained by the different methods of development diminish in the order:—post-fixation physical, alkaline chemical, pre-fixation physical, and ferrous oxalate chemical. Now of these the greatest dissolving action on the silver halide is obviously exercised by the fixing bath in the post-fixation method, and next to this by the alkaline elon-hydroquinone developer (which contains 2.3 per cent Na_2SO_3), but in regard to the elon-acid-silver and ferrous oxalate developers it is difficult or impossible to decide, without direct knowledge, which has the greater solvent or disintegrant action on silver halide. The ferrous oxalate developer contained 0.05 per cent potassium bromide, and the freshly mixed physical developer contained 0.3 per cent silver nitrate, so that, if merely the mass action law applies in this case, it must be concluded that the solubility is lower in the latter solution. The emulsions used, however, contain silver iodide in addition to silver bromide, and there are further considerations including that of the action of the acid contained in the physical developer solution.

A striking dependence of the gamma-ratio of a water-treated and a ferricyanide-treated plate (Eastman Slow Lantern) on the sulfite content of the chemical developer is shown in the following experiment. The developer was: elon, 0.5; Na_2CO_3 , 2.5; Na_2SO_3 , either (i) 7.5, (ii) 2.5, or (iii) none; KBr, 0.1; water, to 100. The standard exposure was given, one plate bathed in distilled water and the corresponding experimental one in 0.5 of 1 per cent potassium ferricyanide for 10 minutes, both washed for 30 minutes in running city water, and developed for 3 minutes at 20° C. The results are as

follows:—(i) 2.24, 0.06; (ii) 2.23, 0.045; (iii) 1.62, 0.004. The gamma ratios are, therefore, 1/19, 1/25, and 1/400, respectively. It is noteworthy that elon without sulfite gives as great a gamma reduction as ferrous oxalate.

Sheppard and Mees,⁴ in experiments on the action of dilute chromic acid solution on the latent image of gelatin emulsion plates, found that when the chromic acid treatment is followed by a bath of sodium sulfite ($N/10$, = 0.63 per cent Na_2SO_3) before development, the rate of appearance of the image and the velocity of development, which are lowered by chromic acid, regain their normal value, and it can then be seen that with increasing times of treatment in the chromic acid, gamma-infinity diminishes and the inertia increases. It seems probable that the restoration of the normal rate of development by the sulfite bath is attributable in part to an incipient solvent action of the sulfite on an outer layer of the silver halide grain. This layer is approximately that through the thickness of which the latent image has been destroyed by the chromic acid; and in this way facility of access of the developer to the residue of latent image (predominantly that of the higher light exposures) that exists beneath is partially restored.

How the ferricyanide effect varies with increasing times in a sulfite-containing developer is shown by an experiment in which Eastman Slow Lantern plates were exposed, treated as before, and developed in: elon, 0.5; Na_2CO_3 , 2.5; Na_2SO_3 , 3.0; KBr, 0.1; water, to 100. (The maximum threshold speed was given by development time of 16 minutes.) Development was given for (i) 1, (ii) 4, (iii) 16, and (iv) 64 minutes, at 20° C. The results are as follows:—(i) 1.38, 0.026; (ii) 2.36, 0.10; (iii) 2.71, 0.25; (iv) 2.83, 0.56; the ratios being 1/53, 1/24, 1/11, and 1/5, respectively. The fog is approximately equal in each case on the untreated and treated plate. The continued action of the sulfite, in exposing the sub-surface nuclei, is thus apparently equivalent to increasing its concentration.

The question arises: Why, if ferricyanide acts only on the nuclei in the grain surface, and if ferrous oxalate or a sulfite-less elon developer acts also only on the grain surface, should any image whatsoever be obtained after such treatment and development? In reply it may be said that the two solutions, ferricyanide and developer, do not act quite similarly. Accessibility of the sub-surface latent image to the ferricyanide solution is dependent mainly on the solubility of silver halide, while in the case of the developer the effect of development fog must be considered. It may be supposed that although after ferri-

⁴ S. E. Sheppard and C. E. K. Mees: The Action of Chromic Acid upon Plates. *Phot. J.* 47: 65. 1907 (Feb.).

cyanide treatment the grain surface is entirely free of nuclei, yet after a time in the course of chemical reduction in the developer a nucleus will form and begin to grow. In the case of a single fog nucleus, growth will be slow, until in growing it extends down and reaches sub-surface nuclei. Then, in consequence of the developer gaining access to these nuclei, the development reaction will be somewhat accelerated. The faint image that appears in such cases as that noted above is thus plausibly explained.

A TENTATIVE CRITERION OF DESTRUCTION OF LATENT IMAGE

Experiments with non-sulfite-containing developers show that the gamma of treated emulsion film increases with time of development up to and beyond the optimum time for maximum threshold speed. The gamma ratio of ferricyanide- to water-treated film rises to a seemingly constant value of about $1/30$ at optimum development. The thought occurred whether, if this ratio were proved constant, it might not be possible to base on it a criterion of destruction of latent image such as the following: When on development in either of two non-sulfite-containing elon solutions, one with and the other without bromide, for times up to and including that for the maximum threshold speed for the untreated material, the greatest gamma of the treated material is not greater than $1/20$ th of that of the untreated material, the latent image may be said to have been destroyed. There are several objections, however. The optimum time of development with non-sulfite-containing solutions is seldom less than one hour, and the stain is then so considerable that density readings are not satisfactory, and, more important than either of these, there is the possibility of a variable degree of nucleus denudation through development fog. On the other hand there is the advantage that the development procedure is as sensitive for the recognition of a trace of latent image as any known.

By sacrificing this advantage it seems possible to eliminate the objections. A low-acidity elon-silver physical developer gives the maximum threshold speed in about 20 minutes, in the case of Slow Lantern plates, and would not appear to introduce any denudation effect other than that due to the solvent action of the solution on the silver halide. This may be assumed to be no greater than that of the (low potential) oxidant bath itself. Applying the modified criterion, it is seen that potassium ferricyanide destroys every trace of image, as judged by examination by transmitted, or for greater sensitivity, by reflected light. This is also true for solutions of

potassium dichromate, and it becomes of interest to see whether it is possible to determine the composition of a chromate-dichromate solution that would, in sufficient time, just destroy a latent image.

It is necessary, first, to standardize the operation of washing after treatment, and the time and temperature of development. It was found that washing for one hour in running city water is adequate, and that it is immaterial whether the emulsion is dried or not before development. The composition of the developer is: elon, 1; citric acid, 1; acetic acid, 5; water, to 100; with one-tenth of its volume of 10 per cent silver nitrate added immediately before use. Development is for 20 minutes, at 18° C.

A noteworthy, though largely subjective, difference between the two methods that have just been suggested is that in the case of the first the developed image scale of the treated emulsion cannot be said to end abruptly at any point, the effect being rather a lowering of gamma than removal of one or more of the lowest fields; whereas in the second, although there is likewise a lowering of gamma of the surviving scale, it is not difficult to see a point at which the image ceases and below which, although there is likewise a lowering of gamma of the surviving scale, no suspicion of further traces of image is felt. For this reason, the gamma ratio is not a suitable means of expressing the reduction of image. In its place, the visual threshold speed number is made use of as in observations for threshold speed (see Chapter VI, p. 118).

Experiments on the action of potassium permanganate solution, with and without acid, for subsequent chemical development, have been made by S. E. Sheppard and E. P. Wightman of this Laboratory. It should be emphasized that the chief source of error in the greater part of all early work dealing with the question of latent image destruction or non-destruction by the action of aqueous solutions, arises from the lack of recognition of the lesser accessibility to the oxidant bath, as compared with the accessibility to the developer, of a possible portion of the latent image, namely, that portion, if any, beneath the silver halide grain surface. Using a procedure by which only the grain-surface latent image is developed, it seems legitimate to conclude, in the event of no image becoming visible, not only that the surface image has been destroyed, but also that the sub-surface image, had it been accessible to the oxidant bath, would likewise have been destroyed. With regard to the action of the higher-potential oxidizing solutions, such as those of permanganate with acid, cupric bromide,

mercuric chloride, or iodic acid, is it not possible that these are able to destroy not only the latent image but also the sensitivity nuclei of high-speed gelatin emulsions, shown by Sheppard⁵ to consist, in all probability, of silver sulfide?

The behavior of visible images of silver and silver sulfide towards solutions of both classes indicates that the silver images are the more rapidly attacked.* Owing to the grain-disintegrating action of any intermediate "bleach" bath, the virtual dispersity of the silver sulfide may be appreciably greater than that of the silver image. If it be assumed that in an exposed gelatin emulsion film the dispersities of the latent image (silver) nuclei and the sensitivity (silver sulfide) nuclei are equal, it would seem to follow that the latent image nuclei should be the more readily removed: and if the writer's view of the dispersity of the latent image nuclei and Sheppard's view of that of the sensitivity nuclei be accepted, the difference in susceptibility to removal is seen to be increased. It may follow, therefore, that with the low-potential oxidizing solutions the latent image may be removed completely but the sensitivity nuclei not at all (in a given time), whereas with the high-potential solutions both kinds of nuclei are speedily removed. Removal of the (comparatively large) sensitivity nuclei may tend to open a way through the surface of the grain and expose the sub-surface latent image to the action of the solution. From these considerations one may explain the lowering of sensitivity by such solutions as destroy the whole of the latent image, and the non-lowering of sensitivity by such as destroy merely the surface latent image.

The concentration speck theory of the mechanism of action of the sensitivity nuclei (Sheppard, Trivelli, and Loveland: see Chapter IV, ref. 37) allows an equally satisfactory explanation.

If both latent image and sensitivity substance consist of silver, only a postulated difference in dispersity remains by which to explain the action of the solutions: the latent image nuclei *must*, in this case, be smaller than the sensitivity nuclei.

SUMMARY

Of those substances capable of converting silver into a salt or salts of silver, a number clearly destroy the low-exposure portion of the latent image, increase the inertia and diminish sensitivity. Others do not clearly destroy the latent image,

⁵ S. E. Sheppard: *Photographic Gelatin. Phot. J.* 65: 380. 1925 (Aug.).

*As a matter of observation. The actual mechanism of the action of a given solution on silver (as a metal) and silver sulfide (as a salt) must be essentially different, and any attempt at comparison of rates of action would scarcely be profitable.

but diminish gamma and do not affect sensitivity. These substances are relatively strong and weak agents for the oxidation, in the wider sense, of silver. The difference in the kind of action on the latent image is found to vanish under development conditions allowing no greater accessibility of the sub-surface of the silver halide grains to the developer than to the latent image destroying solution, substances of the first class merely acting faster than those of the second. The difference in the effect on sensitivity is explained by the greater ability of substances of the first class to oxidize silver sulfide, which is, in all probability, the substance of the sensitivity nuclei in gelatin emulsions. The destruction of the sensitivity nuclei opens the way, it is now suggested, to the destruction of sub-surface latent image, and so accounts for the observed correlation between sensitivity-diminution and definite destruction of latent image (as distinguished from mere lowering of gamma) for ordinary alkaline development. It is suggested that the absence of a visible effect on development in a low-acidity physical developer may be used as a criterion of destruction of the latent image, the destructibility of the sub-surface image being inferred from the destruction of the surface image.

On the Chemical Potential Necessary for the Destruction of the Latent Image

Such an expression as the "destruction potential of the latent image" is convenient, but necessarily vague. On the basis of any of the chemical views (such as Abegg's silver germ theory) of the nature of the latent image, a definite destructive potential is conceivable only when it is possible to fix the concentration of the reaction product in the destructive medium. The expression, however, may be used conveniently to denote the oxidation potential of a solution that just destroys a given latent image under given conditions of volume of solution, temperature, and time of action. Since a rod of silver immersed in a molar solution of silver nitrate has a potential about 1.06 volts higher than the solution, the potential of the solution must be raised by slightly more than 1.06 volts before silver atoms become ionized and pass into the solution. This value is then the destruction potential of silver under the conditions of immersion of the "massive" metal in a molar AgNO_3 , that is, in a somewhat less than molar or normal Ag^+ , solution. Assuming that the latent image consists of silver, and that its maximum amount corresponds to the attachment of a silver atom to each bromine ion in the silver halide surface, it may be calculated that the resulting silver cation concentration in a volume of destroyant solution that is likely to be applied experimentally would be so low that the destruction potential of silver in these circumstances would be lower by at least about 0.3 volt than the 1.06 volts mentioned above: and under extreme conditions, namely, when in presence of a solution which is, and remains, exceedingly low in silver cation content, silver even ceases to be a noble metal.*

Still assuming that the latent image consists of silver, it must be admitted that concerning the *amount* of this invisible silver in relation to that of the visible silver deposit to which it gives rise under given conditions of development, there does not appear to be any direct evidence at all. Some tedious and rather extensive experiments, which are briefly described in the next chapter (pp. 106-8), served only to show that, provided the light-exposure is not so excessive as to produce any trace of print-out image, no more silver can be extracted by a silver solvent from a light-exposed and distilled-water-washed emul-

*This is seen with potassium cyanide solution, though with this the low silver cation concentration is brought about by the approach to complete conversion of ionized silver into complex anion, and not by a scantiness of supply of silver metal.

sion than may be accounted for by certain positive experimental errors. An upper limit to the amount of silver which constitutes a given latent image might perhaps be assigned; such a limit would appear to indicate that the destruction potential of an ordinary latent image should be at least 0.3 volt lower than the potential of massive silver in molar silver nitrate solution.

LITERATURE

As far as the writer is aware, the only direct determinations of the oxidation potential of a solution that is just capable of destroying a latent image have been those of chromate-dichromate solutions by R. Luther. These are outlined in reference 22 of Chapter I. It should be noted that his conclusion, that an equally high oxidation potential is required for the destruction of a latent image as for the bleaching to halide of a printed-out image on the same silver salt, applies to films of silver halide and photohalide, unmixed with gelatin, on glass. The objection, however, of probably unequal accessibility of the latent image to the destroyant solution and to the developer (apparently ferrous citrate with ammonia for the silver chloride, and metol-carbonate-sulfite-bromide for the silver bromide, allowing several hours in each case) applies here as usually in the work of the older literature. The writer finds (see p. 89) that the solution of lowest potential, 1.09 volts, which destroyed only the lowest one of the photometer image fields on silver bromide, rapidly and clearly destroys the latent image on a silver bromo-iodide gelatin emulsion, *if the criterion of destruction tentatively formulated in the preceding chapter (p. 82) be accepted.*

Lüppo-Cramer¹ remarks that "the destroying action of oxidizing or halidizing agents on the latent image does not run parallel by any means to their action on free silver, but the destruction of the image nucleus is dependent on a sufficient isolation of the nucleus in consequence of a specific adsorption displacement rather than upon the oxidation potential of the solution." On the other hand, it is essential, when judging destruction of the latent image, that the accessibility of the latter to the developer shall be not greater than to the oxidizing solution, and it is desirable that its accessibility to the oxidant and to the developer shall be approximately equal, in order that a comparison may be possible of the rate of action of different oxidants. Lüppo-Cramer's method, of securing "nucleus-denudation" and then applying a developer and

¹ Lüppo-Cramer: Über den latenten Schleier. *Z. wiss. Phot.* **23**: 184, 1925 (Apr.).

method of development that is more or less effective for the whole of the latent image, is doubtless preferable in principle to, and possesses advantages over, the writer's method of using a development procedure in which only the surface nuclei are effective. There are also disadvantages, arising out of the greater complexity of Lüppo-Cramer's operations. The writer suggests that the two plans of attack may well be regarded, for the present, as complementary; later, with further data available, a critical comparison may be profitable.

EXPERIMENTAL

Eastman Slow Lantern plates were given a standard exposure to blue light such that seventeen fields of the Chapman-Jones sensitometer would be obtained without pre-treatment on optimum development in Mees's physical developer (p. 121), bathed for 30 minutes in chromate-dichromate solutions which were 0.1 M with respect to K_2O and from 0.1 M to 0.2 M with respect to CrO_3 , washed in running city water for one hour, and developed in the developer for 20 minutes at 18° C. The solutions of 0.2 M down to 0.16 M CrO_3 inclusive, left no image, the 0.15 M solution, a trace, and the 0.14 to 0.1 M CrO_3 solutions, progressively increasing amounts of image. The last-named solution showed no loss of the lowest tablet field, compared with a plate that had been treated similarly but bathed in distilled water instead of in the chromate solution, and only a doubtful diminution in gamma. On several repetitions, the diminution in gamma was not confirmed, and it was concluded that, in 30 minutes, a 0.1 M K_2CrO_4 solution has no appreciable effect on the latent image.

The possibility of an error due to incompleteness of removal of the oxidizing salt from the emulsion film by the washing between bathing and developing must now be considered. It was found by Sheppard, Wightman, and Trivelli,² that "in most cases, for relatively short treatment with not too concentrated CrO_3 —up to two per cent—a bath of five per cent $NaHCO_3$, followed by good washing, is sufficient to remove the CrO_3 ." It seemed probable, therefore, that solutions 0.1 M with respect to K_2O and 0.15 M or lower with respect to CrO_3 would be removed by washing for one hour in running city water. An indirect, confirmatory indication was obtained as follows: Eastman Commercial film and Slow Lantern plates were bathed for twenty minutes in (i) distilled water, (ii) 0.05 M K_2O , 0.1 M CrO_3 , (iii) 0.05 M K_2O , 0.075 M CrO_3 ,

²S. E. Sheppard, E. P. Wightman, and A. P. H. Trivelli: Studies in Photographic Sensitivity. III.—Topochemistry of Development and Sensitizing Nuclei. *J. Frank. Inst.* 196: 653. 1923 (Nov.).

and (iv) 0.05 M K_2O , 0.05 M CrO_3 , washed for one hour in running city water and, after removing surface moisture, exposed uniformly to daylight: *iv* darkened fastest, *i* and *iii* about equally, and *ii* slowest. Alternatively, should, owing to exceptional experimental conditions, potassium dichromate or chromate be retained by the emulsion film in moderate amount, it is difficult to see what effect this could have other than a slight retardation, by reaction with a portion of the silver nitrate, of the physical development.

The action of the solution which is 0.1 M with respect to K_2O and 0.11 M with respect to CrO_3 is interesting and important. This solution produces a diminution in gamma over the upper half of what is the straight-line portion of the curve for the water-treated plate to somewhat less than one-half, with a loss of about two fields at the bottom of the scale, the time of bathing being thirty minutes. When the immersion is increased to one hour and two hours, the gamma is progressively lowered, and the loss of latent image amounts to about three and four fields, respectively. These results are provisionally interpreted as showing that, under the conditions of these experiments, a solution which is 0.1 M with respect to K_2O and 0.11 M with respect to CrO_3 is a destroyer of the latent image, the destruction potential of which, therefore, is lower than the oxidation potential of this solution (and possibly somewhat higher than that of 0.1 M K_2CrO_4).

Luther's solution containing $M/10$ K_2CrO_4 , $M/20$ $Cr_2(SO_4)_3$, $M/16$ H_2SO_4 , and $M/10$ KBr (see p. 18) was now tested as regards its action on the latent image against the same solution with the chromic sulfate omitted. The chromic sulfate used was either in the form of Merck's "white label" chrome alum, which contains a little ferric iron, or of a special solution prepared in this Laboratory and having a lower iron content than any purchasable. In either case, the Luther solution oxidized the latent image on the Slow Lantern plates much faster than did the chromic-free solution, the latter being approximately equivalent in action to a simple chromate-dichromate solution which is 0.1 M with respect to K_2O and 0.13 M with respect to CrO_3 . Destruction of the latent image, in these cases, being progressive, and complete with sufficient time, it is possible only to compare the solutions, and this somewhat unsatisfactorily, as regards rapidity of action. A test of the effect of addition of potassium bromide or sodium chloride, in 0.1 M concentration, to the 0.1 M K_2O , 0.11 M CrO_3 solution, showed a slight slowing of action by the addition of bromide and no change by the addition of chloride.

The accelerating effect, of the chromic sulfate in Luther's solution, on the destruction of latent image, is undoubtedly to be ascribed to the liberation of acid by its partial hydrolysis. Luther had added it in order to have present a definite concentration of the chromate reduction product in the solution, but he seems to have overlooked the fact that the action of the chromic ion of the chromic sulfate in lowering and stabilizing the oxidation potential is swamped by that of the hydrolytic sulfuric acid in raising it. The effect of an addition of a soluble chloride or bromide, especially bromide to a chromate-dichromate solution is to increase its oxidizing (ionizing) action on the silver of a developed or printed-out image. In the case of the assumed silver of the latent image, however, no difference is to be expected, since its amount, it is highly probable, is so minute that the silver ions produced by its oxidation are in such low concentration that they remain in solution as such in presence of any concentration of bromide ions, that is, the solubility product of silver bromide is never reached. (The observed slight retardation of action by the addition of bromide is, for the present, unaccounted for.)

THE DESTRUCTION POTENTIAL OF A LATENT FOG

As is evident from the discussion in the preceding chapter, investigation of the nature of the latent image is rendered difficult by the circumstance that, owing to its possessing a certain depth distribution with respect to the silver halide grain, its accessibility to reagent solutions is not uniform. A latent fog produced by a solution that has no solvent or disintegrant action on silver halide may be expected to be located exclusively on or in the grain surface. In December, 1921, the writer observed that the action of very dilute silver nitrate solution is to produce a fog (as shown on development) which increases continuously with lapse of time after the application of the solution, until it reaches the limit imposed by the silver content of the emulsion. It seemed plausible that a partial unimolecular-layer adsorption of silver ions to the grain surface occurred in the silver nitrate bath, and that these ions, while still adsorbed, became successively discharged (as by the reducing action of the adjacent gelatin, or possibly one of the minor emulsion constituents) to silver atoms. This supposition will be discussed in the following chapter. It suffices for the present that the latent fog produced by treatment with a very dilute solution of silver nitrate should, apparently, consist exclusively of *surface* nuclei. As such, if the nuclei have the same composition as those of the latent light-image, they

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should be destroyed, for any kind of development, by a solution of oxidation potential just sufficient to destroy a latent light-image for pre-fixation physical development.

EXPERIMENTAL

Pieces of Eastman Commercial film were bathed first in distilled water for 15 minutes, then in 0.001 M (\equiv 0.017 per cent) silver nitrate solution without or with addition of acetic acid equal to 0.1 M (\equiv 0.6 per cent), for 15 minutes, and finally in either distilled water or 0.1 M acetic acid, respectively, for 15 minutes. The pieces were occasionally agitated while in the baths, the temperature of which was 20° C. After drying, and leaving in the dark for about 48 hours, the fog with a certain development in elon-hydroquinone was 2.42 in the case of the film that was treated with silver nitrate without acetic acid and subsequently washed in distilled water, and was 0.99 in the case of the other. On bathing in 0.1 M K_2O , 0.11 M CrO_3 solution for 3 hours, washing in running city water for 1 hour, and developing as before, the fog densities found were 0.81 and 0.10, respectively. Treatment with ferricyanide (1 per cent $K_3FeC_6N_6$) for 20 minutes, followed by washing, likewise failed to remove all the latent fog in either case. Contrary to expectation, therefore, no very marked difference in the destructibility of a latent fog produced by non-solvent and non-disintegrant solutions, and that of a latent light-image, with solutions of relatively low oxidation potential, is apparent. It is not quite certain, however, that the fog obtained, after treatment, by chemical development, really represents any portion of the latent fog produced by the silver nitrate. This question is being investigated.

Using physical instead of chemical development, a complete destruction of the $AgNO_3$ -produced latent fog by 0.1 M K_2O , 0.11 M CrO_3 , and a partial destruction by 0.1 M K_2CrO_4 solution, appeared to be shown.

To observe the action of these two solutions on silver element, small amounts of each of two ordinarily pure samples of precipitated silver were boiled, in Erlenmeyer flasks that had been treated with hot acid permanganate,* with (i) distilled water, and the following solutions: (ii) 0.1 M $NaHCO_3$ "reagent," (iii) 0.1 M K_2CrO_4 , and (iv) 0.1 M K_2O , 0.11 M CrO_3 . After three days' boiling, in the case of distilled water and *ii*, no opalescence was formed after addition of a little potassium iodide solution, but in the case of *iii* there was a distinct opalescence. With *iv* this was seen after boiling for

*To remove any trace of retained silver from the glass surface.

only ten minutes. (The test with *iii* was repeated several times, and invariably a little silver was seen to have passed into solution.)

CONCLUSION

Under usual conditions the destruction potential of the latent image is somewhat lower than the oxidation potential of a solution which is 0.1 M with respect to K_2O and 0.11 M with respect to CrO_3 , and available evidence suggests that it may be identical with the potential required for the oxidation (that is, formation of silver cations) in solution, of silver element.

The Silver Germ Theory

In its usual form the "silver germ theory" relates to both the nature and development of the latent image. Sometimes, however, the name is used in relation to development only, the question of whether the latent image is silver from the beginning or whether it merely yields silver by the first action of the developer being left open. This restricted usage is better expressed as the "silver germ theory of development."

LITERATURE

Arago,¹ in 1839, in his report on Daguerre's process, and later Bayeux and others, explained the formation of the invisible image on the daguerreotype plate, in the camera, as the photochemical reduction of a little of the silver iodide to silver, and its development by mercury vapor as the formation of a visible white matt amalgam from the metallic silver.

Ostwald,² although considering it fairly probable that the first product of the action of light on silver halide is a silver subhalide, emphasizes the fact that under the influence of silver nitrate or numerous organic or other substances this somewhat hypothetical subhalide is resolved into metallic silver and normal silver halide. Accordingly, in the wet collodion and gelatin emulsion processes, after immersion in the developer, at those points where light has acted there exists the same solid substance—silver—as that which is being produced in the adjacent liquid by the action of the developer (by its own decomposition in the case of the physical developer, or by reaction of the chemical developer with the normal silver halide). There should occur, therefore, in accordance with the laws governing the separation of solids from liquids, an especially easy precipitation of the developer-produced silver at the light-affected points.

Abegg,³ after a brief survey of the evidence afforded by experiments on the latent image in collodion and gelatin emulsions, by himself, Eder, Abney, Kogelmann, and others, concludes that the developability of the latent image is necessarily bound up with the presence of silver germs, and that the simplest assumption is that these germs are formed directly

¹ J. M. Eder: *Ausf. Handb. Phot.* II. 110. 1895.

² Wi. Ostwald: *Lehrb. allg. Chem.* II. 1. 1078-9. 1893 (Jan. 13).

³ R. Abegg: Die Silberkeimtheorie des latenten Bildes. *Archiv wiss. Phot.* I: 15. 1899 (Jan. 1).

by the light, and not from silver subhalide by the developer, as required by the subhalide theory.

In his paper on "a theory of photographic development," Abegg⁴ traces some consequences of an assumption that the rate of separation of silver germs by the developer, during the time that sufficient halide remains unchanged, is proportional to the total number of germs (including those that may have been formed in the ripening of the emulsion and those produced by light) that are already present at a given moment. He tacitly assumes that development proceeds by the deposition of new silver germs in the immediate vicinity of the original ones, that is, by a great increase in their number but by no increase in size. In Ostwald's explanation it is the size but not the number that increases.

Abegg and Herzog⁵ describe experiments in which a "suspension of so-called molecular silver," obtained by "reduction of silver chloride in the wet way," was added to unripened (or half-ripened), and ripened emulsion, respectively, and the effect of development without, and after, an exposure respectively, observed, as compared with the same emulsion without the addition of free silver. They find that the addition of silver to the unripened emulsion hastens the onset of fog in the developer without greatly affecting the development of the light-image, while a similar addition to the ripened emulsion produces both a strong acceleration of fog and a heightened contrast in the developed light-image.

Eder⁶ describes experiments demonstrating the formation of latent image by camera exposures on wet collodion films containing nitric acid in varying amounts up to a high concentration, and considers these results fatal to the silver germ theory of the nature of the latent light-image.

In a paper on "silver germ action in the development process," Schaum⁷ suggests that the action of the latent image in development is analogous to that of minute particles of a salt in inducing the crystallization of the excess of that salt from its supersaturated solution, as discussed by Wilhelm Ostwald (*Z. physik. Chem.* **22**: 289-330. Apr. 15, 1897). Thus a very dilute, yet supersaturated, solution of metallic silver is formed by the action of the developer, the excess of this silver tending to deposit on the latent image germs (whether these

⁴ R. Abegg: Eine Theorie der photographischen Entwicklung. *Archiv wiss. Phot.* **1**: 109. 1899 (May 1).

⁵ R. Abegg and C. Herzog: Sensibilisationsversuche mit metallischem Silber. *Archiv wiss. Phot.* **1**: 114. 1899 (May 1).

⁶ J. M. Eder: Silbersubbromid im latenten Lichtbilde auf Bromsilber und die Silberkeim-Theorie. *Phot. Kor.* **36**: 277. 1899 (May).

⁷ K. Schaum: Über die Silberkeimwirkung beim Entwicklungsvorgang. *Archiv wiss. Phot.* **1**: 139. 1899 (June 1).

are silver formed directly by the action of light or by the first action of the developer on silver subhalide).

Schumann⁸ states that a glass plate coated in a suitable manner with a very thin film of silver bromide gelatin emulsion may be bathed in fuming nitric acid before development or after fixing without endangering the emulsion film. The developability of the latent image is not injured, nor the developed image completely dissolved. He considers that this proves conclusively that the latent image does not consist at all of metallic silver, and that the developed and fixed image consists of it only in part.

In an article which is mainly a re-discussion of the experimental evidence cited in Abegg's earlier paper (reference 3), Mercator⁹ concludes that "as long as reasons no more cogent than the above are offered me for the existence of silver germs, I consider the subsalt theory simpler and surer than the silver germ theory."

Eder¹⁰ protests against the use of the name *silver germ theory* (Silberkeimtheorie) in the more restricted and less committal sense of silver germ theory of development.

As the outcome of extensive experiments already discussed in small part (pp. 17-8), Luther¹¹ concludes, as regards the latent image, that like the visible image, it probably consists of silver hemihalide, that is of Ag_2Cl , Ag_2Br , or Ag_2I . It must be pointed out that, owing to oversight of certain considerations, Luther's experiments—unfortunately the only ones in the literature known to the writer, in which the action of solutions of measured oxidation potential on the latent image has been observed—do not really lead to the conclusion stated or necessarily stand in opposition to the silver germ theory.

Precht¹² describes experiments on the action of concentrated nitric acid on the latent image of a collodion emulsion film, and from the difficult solubility of the latent image, as compared with the easy solubility of a developed and fixed image, he concludes that the latent image does not consist of metallic silver.

In a note on "Herr Precht and the dead silver germ theory," Eder¹³ considers that Precht and Strecker in writing that "it

⁸ V. Schumann: Zur Theorie des latenten Bildes. *Archiv wiss. Phot.* **1**: 153. 1899 (June 1).

⁹ G. Mercator: Silberkeim- oder Subhaloid-theorie. *Archiv wiss. Phot.* **1**: 199. 1899 (Aug. 1).

¹⁰ J. M. Eder: Die Silberkeimtheorie und Verwandtes. *Phot. Korrr.* **36**: 648. 1899 (Nov.).

¹¹ R. Luther: Studien über umkehrbare photochemische Prozesse. *Z. physik. Chem.* **30**: 628. 1899 (Dec. 30).

¹² J. Precht: Latentes Bild. *Archiv wiss. Phot.* **2**: 4. 1900 (Jan.).

¹³ J. M. Eder: Herr Precht und die todte Silberkeimtheorie. *Phot. Korrr.* **37**: 667. 1900 (Nov.).

seems to us that the silver germ action does not possess an appreciable significance for the development process" (*Archiv wiss. Phot.* 2: 163. Aug., 1900) are but slaying the slain, for he (Eder) had expressed this opinion more than ten years before, and had emphatically restated it in a recent article.

Lüppo-Cramer¹⁴ describes a "fundamental experiment" in which the action of concentrated nitric acid on the latent image of collodion emulsion plates, for post- and pre-fixation physical development, is observed and compared.

In his paper on "solarization in silver bromide films," Weiss¹⁵ describes some significant experiments on the chemical production of germs conferring developability on gelatin-free silver bromide. Using glass with a fine matt surface, he states, "I obtained my most serviceable plates under the following conditions: AgNO_3 *N*/20, HBr *N*/11 to *N*/15, equal volumes; mixing temperature, 17°; height of the layer of silver bromide 'milk' above the plates, 2.5 cm., corresponding to about 12 mg. AgBr per sq. cm. The time of sedimentation varied: I had very good plates that had been 'sedimented' for 8 - 10 days, and the like for 15 - 18 days. The liquid was still somewhat turbid when the plates were 'sucked off.'" To reconvert to bromide any free silver formed by the action of atmospheric dust, ferrous silicate in the glass surface, *etc.*, during these operations, the plates were kept for 24 hours before use in an atmosphere containing bromine and hydrogen bromide vapors, and dried. After bathing in silver nitrate solution and washing for two days to remove largely the adsorbed silver salt, a plate did not darken in a physical developer of either metol with citric acid, or ferrous sulfate, and gum arabic and silver nitrate. After bathing in ferrous sulfate solution and washing, a plate similarly failed to darken on physical development. When, however, a plate was bathed in silver nitrate solution, dried, and bathed in ferrous sulfate solution followed by dilute sulfuric acid, it darkened in the physical developer, even when the concentrations of the silver and ferrous solutions were so reduced that only a barely visible gray deposit of silver resulted before development. A gelatin-free silver bromide film, thus treated, also darkened in a modified *p*-aminophenol chemical developer; and commercial gelatin emulsion plates, thus treated with silver and ferrous solutions, darkened either in an organic chemical or in ferrous oxalate developer. Confirming the experience of Luther, and of Schaum and Braun, it was found that a latent light-image could be developed chemically

¹⁴ Lüppo-Cramer: Zur Silberkeimtheorie der Entwicklung. *Phot. Korrr.* 39: 690. 1902 (Dec.).

¹⁵ H. Weiss: Solarisation in Bromsilberschichten. *Z. physik. Chem.* 54: 305. 1906 (Jan. 29).

on the gelatin-free silver bromide films; and the observation was then made, contrary to expectation, that it could be developed physically. It was found that gold, precipitated in the film of commercial gelatin plates by successive baths of gold chloride and ferrous sulfate, platinum, similarly precipitated by platinic chloride and ferrous formate, and silver sulfide, formed by bathing in very dilute hydrogen sulfide water, cause the film to darken in a chemical developer, that is, act as germs for chemical development. Owing to the difficulty of finding an agent that would reduce their salts in the cold without reducing silver halide also, the effect of germs of rhodium, iridium and other noble metals could not be investigated in the same way.

Solutions of salts of rhodium, iridium, gold, platinum, and platinum-silver were evaporated on opal glass plates, a drop of ferrous formate or formic acid solution was brought on to the deposit, and the plate heated carefully over a small flame. In all cases the spot, even when invisible to the unaided eye, darkened on physical development. Colloidal solutions of arsenious sulfide and platinum, evaporated on the opal glass, darkened similarly in the physical developer, while a colloidal solution of ferric hydroxide did not darken, nor did precipitations of barium sulfate or mercuric iodide. A colloidal solution of platinum, evaporated on a commercial gelatin plate, gave no developable impression on chemical development, obviously because of non-diffusion into the gelatin, and Weiss remarks that this shows how near to each other the germ and silver halide grain must approach to produce chemical developability, and probably why so many failures to observe development with silver germs have been recorded in the literature. He points out that the substances which have been observed to be capable of acting as germs for development are those and only those that are known to form solid solutions with silver. His final conclusion as to the nature of the latent light-image on silver chloride or silver bromide is that it "consists of a solid solution of silver subhalide and/or silver in silver halide. The solid solution is poor in silver subhalide or silver and very resistant towards oxidizing and reducing agents."

In the discussion on Sterry's paper on "the action of oxidizers upon the development of the latent image (a continuation of a paper on the separation of development into primary and secondary action)," Mees¹⁶ suggested that two kinds of nuclei might exist in the plate after exposure. "One nucleus might be an atom of silver and the other the envelope of gelatin in which it was enclosed. It might be that the silver

¹⁶ C. E. K. Mees: *Phot. J.* **47**: 173, 1907 (March).

nucleus could be destroyed by the action of chromate salts and that the latent image formed of the gelatin nuclei could not be so destroyed. On such a hypothesis there would be a primary and a secondary latent image."

Lüppo-Cramer¹⁷ considers that the stability of adsorption compounds of silver halides with colloidal silver and with colloidal gold confirms his earlier conclusion that "the latent photographic image consists of a solid adsorption compound of silver with silver halide."

In a very interesting paper, a translation of which appears in the *Brit. J. Phot.* for Aug. 26, 1910 (pp. 651-3), on "the present status of our knowledge of the nature of the latent image," Luther¹⁸ arranges in columns a series of arguments and counter-arguments between the silver hemi-halide and the silver theories of the composition of the latent light-image. He points out that, in the absence of a definite criterion of chemical combination, the two views are not necessarily mutually exclusive.

Reinders¹⁹ mentions that the latent image is weakened but not quite destroyed by most oxidizing agents, and that attempts had been made to explain the greater resistance towards oxidizing agents, which pure photochloride and the latent image show as compared with silver, by the assumption of a subhalide. After weighing other considerations, he concludes that "the various properties of the photo-halides and of the latent image must be ascribed to the number, form, and dispersity of colloid silver particles in the solid silver halide."

As an outcome of their experiments on the action of light on silver chloride and silver bromide crystals, Lorenz and Hiege²⁰ conclude that "the latent photographic image can scarcely be anything but a mist of extremely fine metallic particles of silver, dispersed in the particular halide."

Assuming that the formation of the latent light-image of a silver halide gelatin emulsion consists in the removal of halogen from the silver halide, Kropf²¹ suggests that thereby the developer is enabled to penetrate the light-affected silver halide grains and accelerate the development reaction. He states that "the cause of developability of light-exposed silver

¹⁷ Lüppo-Cramer: Über die Photohaloide Carey Leas. Auffassung derselben und des latenten Bildes als Adsorptionsverbindungen von Halogensilber und Silber. *Phot. Kor.* **44**: 327. 1907 (July).

¹⁸ R. Luther: Über den gegenwärtigen Stand unserer Kenntnis der Natur des latenten Bildes. *Phot. Rund.* **24**: 221. 1910.

¹⁹ W. Reinders: Die Konstitution der Photohaloide. II. *Z. physik. Chem.* **77**: 356. 1911 (Aug. 1).

²⁰ R. Lorenz and K. Hiege: Ein Beitrag zur Theorie des latenten photographischen Bildes. *Z. anorg. Chem.* **92**: 27. 1915 (June 18).

²¹ F. Kropf: Zur Kenntnis des latenten Lichtbildes. *Phot. Kor.* **56**: 141. 1919 (May).

halide films with chemical developers is not the silver that has been split off, but the halogen, and, logically, one should speak not of a silver, but of a halogen, germ theory."

In the course of a paper on "the relation between sensitivity and size of grain in photographic emulsions," Svedberg and Andersson²² use the words: "if we make the assumption that each halide grain that is struck by one or more than one α -particle has become developable, *i.e.*, has received a silver nucleus large enough to act as a condensation center in the reduction process." and again: "If we make the assumption that a certain minimum number of quanta must strike the grain within a certain maximum area of the grain in order to build up a silver nucleus large enough to act as a reduction center," From this it is clear that the authors consider that the latent image necessarily consists of more than one atom of silver.

After failing to find any satisfactory confirmation of Einstein's photochemical equivalence law, Weigert²³ makes the remark: "There is not yet known to me any real experimental proof that the primary photochemical process leads to the separation of metallic silver, and all conceptions of the photographic processes, that operate with this assumption, appear provisionally therefore still to lack a secure experimental foundation."

In a short paper on the silver germ theory of development, Sheppard²⁴ suggests that the sensitivity nucleus preceding the latent light-image might be "a pleiad of silver germs (perhaps atoms)," and shows how the silver germ and silver subhalide theories of the latent image may be reconciled.

Toy²⁵ assumes "that there exist in the grain particles which are not silver halide, and which are formed during precipitation and subsequent ripening. With any normal exposure (*i.e.*, one which gives a value between 0 and 100 for the percentage of developable grains), it is these particles which form the reduction nuclei, the only action of light being to change their condition in such a way that they become susceptible to the action of the developer." Apparently Toy does not consider that the latent image nuclei differ from the sensitivity nuclei *in chemical composition*. As regards the nature of the nuclei, while mentioning the views of other authors, he leaves the question open.

²² T. Svedberg and H. Andersson: *Phot. J.* **61**: 329-332. 1921 (Aug.).

²³ F. Weigert: Zur Photochemie der photographischen Trockenplatte. *Z. physik. Chem.* **99**: 499. 1921 (Dec. 22).

²⁴ S. E. Sheppard: Die Silberkeimtheorie der Entwicklung. *Phot. Korrr.* **59**: 76. 1922.

²⁵ F. C. Toy: On the Theory of the Characteristic Curve of a Photographic Emulsion. *Phil. Mag.* **44**: 352. 1922 (Aug.).

Sheppard and Wightman²⁶ describe a mechanism by which light may produce, from a colloid silver sensitivity speck, "a nucleus large enough to initiate development for a developer of given reduction potential."

Estermann and Stern²⁷ obtained a minute but calculable amount of silver per given area in the form of a sputtered deposit on carefully cleaned glass plates, and then developed the deposit by means of a solution of hydroquinone, gum arabic, and silver nitrate. Completely invisible under the microscope, the undeveloped deposit was seen by means of the ultramicroscope to possess a discontinuous structure, being composed of individual silver crystals each containing at least 1000 atoms. The separate silver atoms that impinge on the glass surface in the sputtering do not, therefore, remain where they strike but apparently glide along the surface until they come within the spheres of attraction of one another and unite to form larger and less mobile aggregates. Whether or not the *whole* of the silver of the developable deposit is in the form of ultramicroscopically visible atomic aggregates could not, of course, be determined either by direct observation or by calculation. It is evident that if it were shown that no unaggregated silver atoms remained, this would not prove the inability of a single silver atom to act as a nucleus in development. Probably, however, under the conditions of these experiments, the whole of the silver is rapidly aggregated.

Sheffers²⁸ considers that the amount of silver constituting the latent image increases proportionally with increasing insolation, but that there occurs a flocculation or coagulation of the individual silver atoms, producing first a diminution in the rate of increase, and then an actual decrease, of the total active surface of the latent image nuclei ("overexposure" and "solarization," respectively).

In the course of an article on "Pseudo-photographic Effects," Clark²⁹ writes:—"The nuclei in exposed grains probably consist of metallic silver, although nuclei of other elements, such as gold, also act as development centers if they can be formed on the grains. The power of the nucleus to act as a center for development appears to depend on its size, and it is probable that for a given developer under defined conditions it is necessary to attain a certain minimum size of nucleus before development will take place. This has its analogy in other

²⁶ S. E. Sheppard and E. P. Wightman: Note on the Theory of Photographic Sensitivity. *Science* **58**: 89. 1923 (Aug. 3).

²⁷ J. Estermann and O. Stern: Über die Sichtbarmachung dünner Silberschichten auf Glas. *Z. physik. Chem.* **106**: 399. 1923 (Oct. 22).

²⁸ H. Sheffers: Studien über die Solarisation. *Z. Physik* **20**: 109. 1923 (Dec.).

²⁹ W. Clark: Pseudo-photographic Effects. *Sci. Progress* **19**: 266. 1924 (Oct.).

well-known chemical phenomena. For instance, Ostwald found that a certain minimum size of nucleus was necessary to bring about crystallization from a supersaturated solution of a salt. Zsigmondy investigated the influence of colloidal gold particles in bringing about deposition of gold from gold-reduction mixtures, and found that here again a certain minimum size of gold nucleus was necessary before deposition would occur. In this case the size was $2 \text{ m}\mu$, or a particle of $10^{-16} \text{ mg. weight}$.

"Accepting Zsigmondy's value for the minimum size of gold nucleus, and taking $1.66 \times 10^{-24} \text{ g.}$ as the weight of an atom of hydrogen, it is found that this nucleus must contain about 300 atoms of gold. It seems quite probable, then, that the development nucleus of silver in a grain of a photographic plate would be of this order of size. Anyway, it must be a group of silver atoms confined within a certain limited area, and not merely an isolated neutral silver atom.

"If this is the case, then the sensitivity of a silver halide grain in an emulsion will depend on the amount of energy required to give rise to the necessary group of silver atoms. It should be possible to have, say, 100 neutral silver atoms existing on a grain, spread uniformly over its surface at relatively large distances apart, without the grain being developable by a given developer; but if these 100 atoms were grouped together in one cluster in one particular part of the lattice surface, the grain would then be developable."

The bearing of Ostwald's observations with sodium chlorate and of J. Reitstötter's with gold (cited by Zsigmondy), on the behavior of the latent image in development, is probably not as direct as Clark supposes. The particles of gold or sodium chlorate are in Brownian motion, whereas the latent image nuclei are arrested on or in the surface of silver halide particles which are not in similar motion. It would appear that the minimum size or weight which is necessary in the case of a salt or metal particle that is suspended in a supersaturated or colloidal solution of the same or isomorphous salt or metal is really that which, under the experimental conditions, reduces the Brownian motion sufficiently to allow the capture of other particles. Thus it is not a minimum size requirement but, probably, a maximum motion limitation that applies in these instances of nucleus action. The writer suggests that this consideration may help to explain the importance of walls and other surfaces in processes of contact catalysis, the surface acting by immobilizing the true catalyzer particles.

Audubert³⁰ considers that the latent image nuclei produced

³⁰ R. Audubert: La photovoltaïcité des halogénures d'argent et le mécanisme de formation de l'image latente en photographie. *Comp. rend.* **179**: 1046. 1924 (Nov. 17).

by light consist of metallic silver atomic aggregates in colloidal form. In development these nuclei play an analogous rôle to that of small crystals in the crystallization of a supersaturated solution.

In a review of "recent investigations on the photographic process," Meidinger³¹ deals with the recent literature of the question of the amount of silver composing the normal and solarized latent light-image.

The same author³² determines the density curve of two brands of emulsion (Agfa plates) for light of 436 m μ , and development with rodinal, by the two methods of grain counting and silver titration, and concludes from the results that "in certain circumstances one silver atom (corresponding to one quantum) may make a grain developable. On the other hand, with one thousand silver atoms per grain, not all the grains are developable."

In an explanation of the Villard effect, Arens³³ supposes that the (uncoalesced) image nuclei initially produced by white light are characteristically *larger* than the similar nuclei of X-rays.

In a note on the function of gelatin in development, Slater Price³⁴ suggests that the protective action of gelatin, by preventing the agglomeration of silver amicros to larger particles, may tend to reverse the reduction action in development, and thus favor an increase in the possible amount of supersaturation of silver before deposition takes place.

Eggert and Noddack³⁵ conclude, *inter alia*, that in the case of a pure silver chloride emulsion prepared and used by them in an investigation, one molecule of silver chloride is decomposed for each quantum of ultra-violet radiation of wavelength 365 m μ that is absorbed.

Schmidt³⁶ considers that under the action of light an electron in the silver bromide crystal lattice passes from a bromine ion to a silver ion, giving rise at a certain point of the lattice surface, to an atom of bromine and an atom of silver. The former may volatilize, and the latter is adsorbed by a neighboring bromine ion. Thus there is produced a "breach" at which the developer can commence its attack on the grain.

³¹ W. Meidinger: Neuere Untersuchungen über den photographischen Prozess. *Phot. Ind.* **22**: 1084. 1924 (Dec. 1).

³² W. Meidinger: Untersuchungen über die photographische Schwärzungskurve. *Z. physik. Chem.* **114**: 89. 1924 (Dec. 13).

³³ H. Arens: *Z. physik. Chem.* **114**: 370-4. 1925 (Jan. 20).

³⁴ T. Slater Price: Note on the Function of Gelatin in Development. *Phot. J.* **65**: 94. 1925 (Feb.).

³⁵ J. Eggert and W. Noddack: Zur Prüfung des Quanten-Aequivalentgesetzes an einigen Halogensilberemulsionen. *Z. Physik* **31**: 922. 1925 (April 14).

³⁶ H. Schmidt: Die Reifung der photographischen Emulsionen vom Standpunkt der Ionendeformationslehre. *Z. wiss. Phot.* **23**: 201. 1925 (June).

Sheppard, Trivelli, and Loveland³⁷ advance the "concentration speck theory," in which it is suggested that the function of the sensitivity specks is to collect about them the silver atoms produced by the photochemical decomposition of silver halide. "There is no catalysis of photochemical decomposition, but only an auto-catalyzed orientation of the decomposition." "The action of light itself can supply centers in the absence of foreign nuclei."

The writer³⁸ has expressed the opinion that "the unit of latent image (or latent fog) in its most effective usual form for chemical or physical development is a single silver atom at rest." At the time this note was written no work had been done on the present chapter, and he did not realize that a silver atom as the unit constituent of the latent image of a minimum exposure had been suggested by Mees in 1907 and maintained recently by Meidinger and other German workers. The necessary "at rest" condition, however, had apparently not been stated. The writer arrived at the monatomic, as opposed to the essentially polyatomic, view on purely chemical grounds, ignoring all considerations of the probable mechanism of formation of the latent image and considering only the scantier but more direct evidence of its nature when formed.

In a paper on "Solarization," Slater Price³⁹ explains an experimental inference of Lüppo-Cramer's that agglomeration may increase the rate of development "by the assumption that the agglomeration is that of amicros of a size insufficient to act as nuclei, to particles sufficiently large to act as nuclei."

Wightman, Trivelli, and Sheppard,⁴⁰ in discussing the action on the latent image of a pre-exposure to light plus hydrogen peroxide treatment, make use of the hypothesis that "the light not only produces a developable latent image, but also an undevelopable one for the developer used, in other words, some of the sensitivity spots are raised almost, but not quite, to the developable state. The hydrogen peroxide not only carries these over, but creates its own proportion of developability as well from other sensitivity spots."

Beginning an explanation of the varying sensitivity of grains on the basis of the minimum size requirement of the latent image nucleus, F. C. Toy⁴¹ writes: "Suppose we denote various-sized specks by all values between 0 and 100, and let us

³⁷ S. E. Sheppard, A. P. H. Trivelli, and R. P. Loveland: Concentration Speck Theory. *J. Frank. Inst.* **200**: 73. 1925 (July).

³⁸ E. R. Bullock: Latent Image and Solarization. *Brit. J. Phot.* **72**: 494. 1925 (Aug. 14).

³⁹ T. Slater Price: Solarization. *Brit. J. Phot.* **72**: 506. 1925 (Aug. 21).

⁴⁰ E. P. Wightman, A. P. H. Trivelli, and S. E. Sheppard: Effect of Pre-exposure to Light. *J. Frank. Inst.* **200**: 344. 1925 (Sept.).

⁴¹ F. C. Toy: The Riddle of the Photographic Plate. *Phot. J.* **65**: 31. 1925 (Oct.).

assume that in order to be developable a grain must have on its surface a speck of silver or silver sulfide, size 100, or larger." Toy thus suggests that the minimum latent nucleus may consist not only of either 100 atoms of silver or 100 molecules of silver sulfide but of one molecule of silver sulfide with 99 atoms of silver, 2 molecules of silver sulfide with 98 atoms of silver, or similarly to 99 molecules of silver sulfide with one atom of silver.

Kögel and Steigmann⁴² consider that very fine germs of silver or silver sulfide, when slowly formed in contiguity with silver halide, confer the three qualities of sensitivity, fog, and optical sensitization.

In a review of the recent development of the theory of the photographic process, Noddack⁴³ states that the majority of the investigations indicate that the latent image is not to be attributed to a structural alteration of the silver halide grains but that it consists of elementary silver which "is separated in atomic form."

Nature of a Latent Fog.—The well-known phenomenon of the gradual growth of general fog on the prolonged storage of any development emulsion, whether on glass, film, or paper, possibly bears on the complexity of the latent image. The growth of latent fog is accelerated either by washing in distilled water and drying, or by bathing in very dilute silver nitrate solution, washing in distilled water, and then drying, before storing. In December, 1921, some experiments in this connection seemed significant, and these, with other available evidence, led the writer to the view that a single silver atom (not ion) attached on, or in, the surface of the silver halide grain may constitute a nucleus for development.

A typical experiment is as follows: A $2\frac{1}{8}'' \times 3\frac{1}{4}''$ piece of Eastman Commercial film of recent date was bathed in several changes of distilled water for fifteen minutes, then in 0.001 *M* silver nitrate with occasional agitation for fifteen minutes, and in several changes of distilled water for fifteen minutes, with the baths kept at about 20° C. On development in a certain elon-hydroquinone developer for a fixed time at 20° C., the film showed slight or doubtful increase in fog over a film that had been bathed in changes of distilled water for forty-five minutes. A number of pieces of film were now treated simultaneously with silver nitrate as described, and left to dry spontaneously in the darkroom. In the first hour the fog increased 0.21, and in the seven succeeding hours the increases observed were successively 0.15, 0.12, 0.15, 0.14,

⁴² G. Kögel and A. Steigmann: Ueber die Identität zwischen Bromsilber- und Farbstoffsensibilisatoren. *Phot. Ind.* **24**: 32. 1926 (Jan. 11).

⁴³ W. Noddack: Neuere Entwicklung der Theorie der photographischen Prozesse. *Phot. Ind.* **24**: 56. 1926 (Jan. 18).

0.20, 0.14, and 0.33. The pieces of film were almost "air-dry" at the end of the third, and quite so at the end of the fourth, hour. The growth of latent fog is thus seen to be not very different in the water-swollen and in the air-dry emulsion film. This result was confirmed in other and more extended experiments; and it is concluded that the rate of growth of latent fog in a silver nitrate treated emulsion film is sensibly constant both during drying and subsequently on storage until the fog density obtained approaches that given by the same development of the optimum light action. Care was taken to avoid any error due to the appreciable optical sensitizing effect of the treatment.

It is necessary to consider some plausible mechanism of the growth of latent fog that could occur equally in the water-swollen and in the air-dry gelatin emulsion film. The silver halide of the prepared emulsion carries adsorbed bromine ions. These are partially removed by the first washing with distilled water. On bathing in the silver nitrate solution, silver ions tend to be adsorbed both by the bromine ions in the lattice surface and by the remaining bromine ions that are themselves adsorbed by the silver ions in the original lattice surface. There is also an effect of the silver nitrate on the gelatin: when the solution has a hydrogen ion concentration below that of the iso-electric point of gelatin, silver oxide will be retained to some extent even after washing in distilled water. When acetic acid was added in $0.1M$ concentration to the silver nitrate solution and the second washing was in $0.1M$ acetic acid, the fog-increase observed was much lower, but it appeared sensibly constant during drying, and subsequently, as in the case when no acid is present. It would seem, therefore, that retention of silver oxide by gelatin is not material in regard to the growth of fog. There can be but little question that silver ions in contact with gelatin are, one by one, reduced to silver atoms. The adsorbed silver *ions*, therefore, become attached silver *atoms*; unless these atoms become freed from the lattice constraint at the moment of formation and then segregate to embryonic crystals of metallic silver. In the absence of evidence it seems simpler to assume that this motion of silver atoms to form aggregates does not occur. In the experiments of Estermann and Stern (ref. 27) the conditions are perhaps essentially different. There the silver atoms were already in motion, and when their motion was interrupted, the tendency of the glass surface to hold them at the points of impact was presumably less than that of a silver halide surface to hold silver atoms at the points of attachment.

It seems plausible to suppose that the latent fog produced by silver nitrate treatment is similar in nature to the latent image produced by light. The principal differences would seem to be that whereas the former consists essentially of unaggregated silver atoms on the silver halide grain surface, the latter consists also of atomic aggregates (increasingly so with the exposure) and is not situated exclusively on or in the grain surface, but (likewise increasingly with the exposure) also beneath the surface. In order to have proof that the image nuclei of low light-exposures are single atoms of silver, it would be necessary to know (1) that these nuclei are of the same nature as those produced by silver nitrate treatment and (2) that the latter are single atoms of silver. Direct and conclusive evidence on these two points is, almost necessarily, lacking.

Attempts at the Analytical Detection of Free Silver in Exposed Emulsions.—When a development emulsion is exposed to light until it becomes visibly discolored, then washed with distilled water, and extracted with a silver solvent, the presence of free silver (or its equivalent as subhalide) in the exposed emulsion is shown by the obtaining of a stronger reaction for silver than is given by a similar extract of an equal amount of the unexposed emulsion. In view of this indication of the presence of what might be called a statistical excess of silver in a printed-out and washed development emulsion, the writer, in experiments in 1922 and 1923, sought to answer the question of whether it is possible to detect silver analytically in an invisible, latent image. The exposure given was of the order of one-tenth of that required for a barely perceptible print-out effect, thus corresponding usually to some point in the overexposure portion of the density curve.

Early in the experiments it was found, not only, as expected, that all development emulsions tried yield a soluble halide to distilled water, but also, as was not expected, that, after washing with distilled water, all these emulsions yield a silver salt to a dilute acidified potassium permanganate solution. The amount of this silver appears to increase with the time of storage of the plate. Less silver is extracted from a pure bromide than from a bromo-iodide emulsion, and less with unacidified than with acidified permanganate.

Using pure bromide emulsion plates, and unacidified permanganate, the following procedure was tried. An exposure of about one-tenth of that required for the first visible discoloration was given, and the exposed with a similar unexposed plate washed for one hour in twelve changes of distilled water, and the plates then bathed, separately, in the minimum volume

of 0.1 per cent potassium permanganate for one hour, at 20° C. or somewhat below. Each extract was poured through a well-washed filter (to keep back particles of emulsion), and the filtrate boiled down to about one-fourth its volume, and then decanted or filtered from the separated manganese dioxide. When cold, a little sulfuric acid and one drop of 5 per cent potassium bromide solution were added, and the liquids observed for opalescence after 20 minutes. The manganese dioxide was dissolved by means of sulfuric and pure oxalic acid, and tested similarly for silver. Usually, the solution showed a trace of silver, and the manganese dioxide none, from the exposed and unexposed emulsion alike. When, instead of prepared plates, an experimental pure bromide emulsion was made, coated on the inside of glass trays, exposed, washed, and extracted, similarly indecisive results, as between exposed and unexposed emulsion, were obtained.

The effect of fixing the plates, before extracting them with the silver solvent solution, was now tried. Fixation was in either (1) boiled solutions of hypo and sodium sulfite in various ratios, (2) a boiled solution of sodium sulfite containing about 16 per cent of the anhydrous salt, and (3) potassium bromide solution containing 50 grams of the salt in 100 c.c. of the solution. Various emulsions were used. The solution 2 was very slow in clearing bromo-iodide emulsions, but by renewing the solution its use was possible in all cases, and it has the advantage over the other solutions of a minimum solvent action on free silver. With 3 prior hardening of the emulsion, as by means of formalin or chrome alum, was necessary, and successive baths of the concentrated bromide solution had to be used before the emulsion was permanently cleared, that is, before it ceased to become opalescent on washing. The silver halide having been removed, acid permanganate could be used to extract the free silver. As with the previous procedure, however, the usual result, in many experiments, was the finding of a trace of silver in both exposed and unexposed emulsion.

Of the several sources of error, one that was, at first, unsuspected, is the withdrawal from solution and retention of silver by a glass surface. This effect was found to vary with the kind of glass and with the nature of the silver solution, although every kind of glass and silver solution that was tried showed it in some degree. The retained silver seems perfectly resistant to washing with distilled water but is readily and completely removed by dilute permanganate with sulfuric acid. The form in which the silver is retained by the glass—whether, for example, as metal, oxide, or silicate—was not

determined. A possibly analogous effect, the retention of mercury from a dilute mercuric chloride solution by glass, has been described by K. C. Browning (*Trans. Chem. Soc.* **111**: 239-40. 1917).

With an exposure of about 10 times that required to give a just perceptible discoloration of an emulsion, no difficulty was experienced in observing the higher free silver content of the exposed, as compared with the unexposed, emulsion. An approximate determination of the free silver in a print-out image on a development emulsion thus seems possible, but this would not necessarily have any bearing on the composition of the latent image.

As regards the traces of silver so consistently found on washing and extracting unexposed emulsions, it is not impossible that their principal source, at least in certain of the experiments, is the silver sulfide of the sensitivity nuclei.

Variation in the Destructibility of the Latent Image according to the Particular Silver Halide in which it is Formed.—The relative ease of destruction, by an oxidizing agent, of the latent image on different silver halides has been recorded in only very few instances in the literature. Abney, with collodion dry plates, which were washed between exposure and treatment with the oxidizing solution, found a more rapid or more complete destruction of the latent image in pure iodide than of a similar image in pure bromide (p. 14). Luther, with films of medium-free silver halide on glass, found that a solution of about one-fourth of a volt higher oxidation potential was required for the destruction of the latent image in pure chloride than for a similar image in pure bromide (pp. 17-8). Sheppard, Wightman, and Trivelli found a much greater resistance of the latent image in a pure chloride, as compared with a similar image in a bromo-iodide, gelatin emulsion (p. 39). It should be noted, however, that what is actually compared in these experiments is the rate of destruction of the latent image, or, more strictly, of such portions of the latent images as are effective in the development given. Notwithstanding the work of Luther, which has been discussed in Chapter III, it does not appear to have been shown that there is any difference between the oxidation potential required to destroy a latent image in one halide and that in another. Further investigation is required. Meanwhile, the fact that the rate of destruction has been shown to be greatest in silver iodide and least in silver chloride demands consideration. Since the iodides in general have a stronger tendency than the chlorides to the formation of *perhalides*, it seems not unreasonable to suppose that the

reverse might be the case as regards their tendency to the formation of *subhalides*. Thus, silver subiodide might well be less stable than silver subchloride, in harmony with the greater rapidity of its decomposition by an oxidizing agent. The subhalide theory of the nature of the latent image, however, in the present state of our knowledge or lack of knowledge of the silver subhalides and the constitution of chemical compounds, can be neither proved nor disproved. As an alternative explanation, which it might prove possible to test experimentally, it is suggested that the more rapid destruction of the latent image in silver iodide is due to the liberation of free iodine which then combines with the silver of the latent image, these two reactions together being faster than the direct reaction of the oxidizing agent with the silver of the latent image. In the case of a latent image in silver chloride, the intermediate liberation of appreciable halogen (except with solutions of the highest oxidation potential) generally does not occur.

The Minimum Size of the Latent Image Nucleus.—If a slow emulsion, such as Eastman Slow Lantern, be impressed with low light-exposures, development for the optimum time in alkaline elon may reveal light-action as a visible scale over an exposure range of as much as 1:20 while at the same time an acid elon physical developer used before fixation fails to show any density difference due to light-action over this range in any time of action. The writer feels that this is difficult to explain on the basis of the atomic aggregate view of the minimum latent image. The light-action being low, it must be supposed that the nuclei are quite near the grain surface, and no considerable difference in accessibility to the respective developers that would account for the result can be assumed. If a minimum size or weight is the necessary and sufficient condition for developability, why is the nucleus that is just effective with the chemical developer not effective also with the physical developer? In both cases it is supposedly reached by a supply of metallic silver, although in the form of particles of probably different average degree of aggregation. Variation of the nucleus minimum size or weight requirement with the reduction potential of the developer was suggested in 1923 by Sheppard and Wightman (ref. 26). Such a variation must be admitted; and the principal question remaining is whether the minimum latent image for the most effective developer and method of development is a single silver atom or an aggregate of perhaps 300 atoms (of silver, or of silver sulfide and silver together).

The Silver Sulfide Germ Theory

The expression "silver sulfide germ theory" is not unambiguous. As used originally, it denotes the view that the thio-sulfate-fixed latent light-image nucleus in silver halide gelatin emulsion film consists of silver sulfide. It might, however, be taken to mean the view that a nucleus of silver sulfide functions in development equivalently to one of silver, or, again, the view that the latent image nucleus in a gelatin emulsion consists of a sensitivity speck (molecular aggregate) of silver sulfide surrounded by silver atoms.

LITERATURE

In a note on "The Silver Sulfide Germ Theory of Herr Precht," Eder¹ comments briefly and unfavorably on J. Precht's view that the latent image (for physical development) on an exposed and thiosulfate-fixed silver bromide gelatin emulsion plate consists of silver sulfide.

Weiss² records that silver sulfide, formed either by bathing in very dilute hydrogen sulfide solution or by moistening and bringing for a moment into an atmosphere of hydrogen sulfide, causes commercial gelatin plates to darken in a chemical developer. The experiment being successful in total darkness, it was clear that the effect was not due to the known red sensitivity produced by silver sulfide.

Steigmann³ discusses the further toning of sulfidized silver images by means of gold or platinum baths such as are used for toning printing-out papers. He remarks that it is known that silver sulfide germs promote the reduction of silver as effectively as do silver germs.

It is not clear to the writer by what process the silver images were sulfidized. If by means of hypo-alum, it is probable that appreciable silver was left unchanged. This would invalidate Steigmann's conclusion as to the nucleus action of silver sulfide in a gold or platinum toning bath. He does not give any literature reference for the statement concerning silver sulfide germs.

Referring to the sensitivity specks which he shows to consist of silver sulfide, Sheppard⁴ writes: "It must be remem-

¹ J. M. Eder: Die Schwefelsilber-Keimtheorie des Herrn Precht. *Phot. Korr.* **37**: 667. 1900 (Nov.).

² H. Weiss: *Z. physik. Chem.* **54**: 328. 1906 (Jan. 29).

³ A. Steigmann: Reaktionen des Schwefelsilbers. *Phot. Ind.* **23**: 541. 1925 (May 18).

⁴ S. E. Sheppard: *Colloid Symposium Monograph* **3**: 97. 1925 (June).

bered that these nuclei of Ag_2S are themselves contributing to the reducibility and developability. They have only to add around one of them a sufficient increment of silver atoms to ensure developability of the grain. If they are themselves increased, in sensitizing, above a certain size, they can lead, as the writer and his colleagues have already pointed out (*Phot. J.*, **65**: 136, 138), to spontaneous developability or 'latent fog.'

"It will be seen from this that the 'latent image' must actually consist of colloid silver on nuclei of silver sulfide."

Steigmann⁵ describes the use and the results obtained by the use of the Lumière silver-or-mercury intensifying solutions for the further toning, intensification, or further toning and intensification of sulfidized silver images (prints or negatives).

Sheppard⁶ mentions that it is known that silver sulfide is capable of acting as a nucleus in silver reductions, and states his view that in exposure a "sensitivity center" of silver sulfide grows by local accretion of silver atoms till it becomes a "developable center."

Toy⁷ writes: "Now one other substance besides silver which will give developability is silver sulfide—the substance of the vital specks if Dr. Sheppard is correct—so that as long as a speck is large enough it will cause developability of the grain on which it is, independently of whether it is all silver, or silver sulfide, or part of each."

Kögel and Steigmann⁸ consider that very fine germs of either silver or silver sulfide, when slowly formed in contiguity with silver halide, confer the three properties of sensitivity, fog, and optical sensitization.

Sheppard⁹ points out that the insufficiency of high-speed sensitizing with soluble sulfides, as compared with the indirect action of such substances as the thiocarbamides, is associated with their greater tendency to fog, *i.e.*, with their much greater rapidity of action and consequent formation of over-large nuclei.

THE EFFECTIVENESS OF SILVER SULFIDE NUCLEI IN DEVELOPMENT

In the foregoing references in which this subject is considered, the authors agree that silver sulfide is developable, in other words, that it can act as a nucleus or germ for the de-

⁵ A. Steigmann: *Atelier Phot.* **32**: 72-3. 1925 (July).

⁶ S. E. Sheppard: *Phot. J.* **65**: 386-7. 1925 (Aug.).

⁷ F. C. Toy: *Phot. J.* **65**: 34. 1925 (Oct.).

⁸ G. Kögel and A. Steigmann: *Phot. Ind.* **24**: 33. 1926 (Jan. 11).

⁹ S. E. Sheppard: *Brit. J. Phot.* **73**: 34. 1926 (Jan. 15).

position of silver from a solution in which the metal is being liberated by the slow reduction of one of its salts. Sheppard, however, points out a probable dependence of the effectiveness of silver sulfide in development on the size of the nucleus, a certain minimum aggregation being required to constitute an "over-size sensitivity speck" of latent fog. The action of similar silver and silver sulfide nuclei may, therefore, differ only in degree.

In February, 1924, the writer observed that the effect of treating a plate that had been exposed and then fixed by hypo, by any one of the three principal sulfur-toning processes (bleach-and-sulfide, polysulfide, and hypo-alum) was apparently to destroy the latent image for subsequent physical development, but that a selenium toning treatment, using a solution obtained by dissolving selenium in excess of sodium sulfite solution, did not completely destroy the latent image. These experiments, however, were inadequate in two respects: only hypo was used as fixing agent, and the effects of diminishing the acidity of the physical developer and increasing indefinitely the duration of development were not tried. Still it may be recorded that bathing in dilute, polysulfide-free sodium sulfide solution was not found to produce any very appreciable diminution of the latent image on the fixed plate, for subsequent standard physical development. These results, such as they are, suggest that silver sulfide is considerably less effective than is silver in physical development. If, however, the silver sulfide could be reconverted to silver, and were then found to possess the original developability, the conclusion would be strengthened. This has not been tested satisfactorily, owing apparently to the loss, by passing into solution, of appreciable fractions of the very small total of the image material.

In comparing the developability of silver and silver sulfide, the purity of the latter must not be neglected. A visible image or invisible molecular aggregate of silver sulfide might contain a few molecules of silver selenide or telluride, whose action in development is possibly quite different. The presence of free silver or free sulfur, or both, is not improbable. Disregarding free sulfur, whose action seems negligible under ordinary conditions, the possible presence of free silver must be given careful consideration. This will be done in experiments now planned, and the matter will be discussed later. Meanwhile, it seems reasonable to conclude, provisionally, that, for equal size of particle, silver sulfide is not nearly as effective a nucleus in development as is silver.

PRODUCTION OF LATENT FOG BY THE
MORDANTING OF A BASIC DYE ON SILVER SULFIDE

In discussing his finding that the material of the sensitivity centers is silver sulfide, Sheppard¹⁰ writes: "It is not impossible that prior to exposure the 'sensitivity centers' may have some accretion of metallic silver atoms, but this does not appear essential. In other directions also this result appears likely to help clear up certain vexed problems. The mordanting action on silver sulfide of basic dyes is probably not without importance for certain desensitizing and fogging actions." Whether basic dyes, as a class, will mordant on to silver sulfide more intensely than on to silver bromide or iodide is a matter concerning which there is, *prima facie*, a sharp difference of opinion.

In a contribution to a discussion held by the Faraday Society in May, 1923, the writer¹¹ states, "Considering, for example the four silver salts, cyanide, iodide, chloride, and sulfide, it is well known that the solubility of silver cyanide in *N* KCN solution is greater than that of silver iodide in *N* KI, this than silver bromide in *N* KBr, this than silver chloride in *N* NaCl and this again than silver sulfide in *N* Na₂S. As regards the three last-named silver salts, as ordinarily prepared as images in gelatin by precipitation with an excess of the corresponding potassium or sodium salt, this is the order of their decreasing mordanting power for basic dyes." According to this statement it appears that basic dyes will mordant *less* intensely on to silver sulfide than on to silver bromide or iodide, assuming that the silver salts are carrying the corresponding anion adsorbed.

Robach,¹² in "A New Method of Dye-toning," describes his discovery of "the silver sulfide dye-mordantive process." He recommends (a) bleaching in a solution of ammonium dichromate, sodium chloride, and hydrochloric acid, and rinsing, (b) clearing in 3 per cent sodium sulfite solution, and (c) "re-developing" in either sodium sulfide solution, a solution of "potassium sulphuret" with hypo, or a solution of sodium thioantimoniate (Schlippe's salt) with ammonia, (d) washing for about five minutes, (e) drying, and (f) bathing in the solution of the basic dye. It must be pointed out, however, that, according to this procedure, the sulfidized silver image will always contain a certain amount of a chromium compound,

¹⁰ S. E. Sheppard: *Phot. J.* **65**: 387. 1925 (Aug.).

¹¹ E. R. Bullock: *Trans. Faraday Soc.* **19**: 397. 1923 (Oct.).

¹² M. Robach: *Brit. J. Phot.* **70**: 363-4. 1923 (June 15); also **71**: 34, 183. 1924.

and, if darkened with thioantimoniate, will contain in addition a certain amount of an antimony sulfide.*

Seyewetz¹³ writes: "Our trials have not confirmed those of Robach, and, working as the author indicates, we have not found in silver sulfide even a feeble mordant for basic dyes."

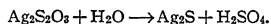
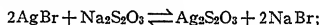
Regarding this apparent *impasse*, the writer ventures the opinion that basic dyes do not mordant appreciably on to pure silver sulfide that has been formed by means of an excess of a soluble sulfide, and that Robach's positive results were due to his use of baths giving a final image of silver sulfide associated with an appreciable amount of some other substance.

This conclusion, however, does not necessarily apply to silver sulfide that has been formed, not through excess of a soluble sulfide but by a mechanism similar to that which has been traced by Sheppard for the formation of the sensitivity specks of high-speed gelatin emulsions. The writer has observed** a conversion of silver bromide to silver sulfide by the action of a very dilute solution of sodium thiosulfate. It was not known whether this observation was new, but it may have some practical value as indicating a method for the sulfur toning of silver images by means of odorless solutions. Silver images on cinematograph positive film were converted to silver sulfide by this method (see foot-note), immersed briefly

*Regarding the mordanting of basic dyes on to images containing a sulfide of antimony, tin, or arsenic, the writer found that "there are a variety of ways in which an image of silver can be converted into one which is colloid in character; and when this colloid is such that it persistently carries a pronounced negative charge, then the image which it comprises will mordant basic dyes, e.g., the images obtained by bleaching in ferricyanide-bromide and darkening in solutions of soluble thioarsenates, thiostannates, or thioantimonates in which solutions the concentration of electrolytes is not too high. A suitable bath is a solution containing 0.1 per cent of the sulfide of arsenic, tin, or antimony, respectively, dissolved by means of a slight excess of ammonium sulfide."

¹³ A. Seyewetz: *Bull. soc. franç. phot.* 12: 204. 1925 (Sept.).

***"While considering the properties, as published in the literature, of silver thiosulfate it seemed probable from the value of this salt's solubility and from its high tendency to spontaneous decomposition, that an exceedingly dilute solution of sodium thiosulfate might be effective for the conversion of silver bromide to silver sulfide, the conversion taking place in two stages as represented by the equations:



Upon experiment, it was then found that a very dilute sodium thiosulfate solution does tone an image of silver bromide. Prints were bleached to silver bromide, some completely by means of bromine water and others incompletely by the usual ferricyanide-bromide bleach, washed thoroughly, and then immersed in large volumes of very dilute sodium thiosulfate solutions and left at room-temperature (about 20° C.). It was eventually seen that concentrations of sodium thiosulfate higher than about 0.001 per cent $\text{Na}_2\text{S}_2\text{O}_3$, $5\text{H}_2\text{O}$ are inadmissible, owing to incipient dissolution of the image. With concentrations of 0.001 per cent and 0.0005 per cent, toning was complete in about two days. Tests indicated that the toned image was substantially silver sulfide; its color, however, was very yellowish compared with that given by normal 'redevelopment,' and there was considerable 'bronzing' of the shadows. (Similar 'bronzing' of the shadows was observed when using very dilute sodium sulfide solutions for darkening and leaving the prints at rest in the solutions; while with periodic handling of the prints no 'bronzing' occurred, even in the sulfide bath having the lowest concentrations—0.01 per cent Na_2S —tried.) With concentration of sodium sulfide much below 0.0005 per cent, the toning action was seen to be exceedingly slow. The effect of raising the temperature is to shorten the time of toning; for example, 0.001 per cent $\text{Na}_2\text{S}_2\text{O}_3$, $5\text{H}_2\text{O}$ solution at 70° C. was found to require only about two hours."

in ten per cent hypo to remove any unchanged silver bromide, washed, bathed in dilute acetic acid solutions of the basic dyes, malachite green, methyl violet, and safranin A, and well washed. Each dye mordanted unmistakably on to the image. Because of the great transparency of this sulfided, compared with the merely bleached, image it was difficult to make a comparison by inspection of the dye deposited in the two cases: the amount is possibly of a similar order. It may be concluded that silver sulfide formed indirectly as described and having presumably neither sulfide nor silver ions adsorbed, is a decided mordant for basic dyes and may be a practical one. It is to be inferred that the (somewhat similarly formed) silver sulfide of the sensitivity specks is likewise a mordant for basic dyes.

It seems very probable that the molecular aggregates of silver sulfide, constituting the sensitivity specks or nuclei, the formation of which has been traced by Sheppard, suffer a further slight and superficial chemical reduction to elemental silver in the ripening process. Each of the silver salts, bromide, iodide, and sulfide, in a high-speed emulsion, undergoes a degree of chemical reduction by the gelatin, but in the case of the more soluble salts the liberated silver atoms may be formed at points comparatively so remote from the grain surface that they do not become attached to it, while with the much more insoluble silver sulfide, such trace of silver as is liberated may be formed so near the surface of the particle that it is captured and retained by it. If this retention be admitted, then apparently the silver sulfide particle should be a completely effective nucleus for physical development, and a less effective nucleus for chemical development since the silver atoms are not in actual contact with a readily available source of silver (such as silver bromide is in a chemical developer). The physical development of a high-speed emulsion is never very satisfactory, because of the heavy fog that usually appears before an adequate gamma is obtained. This experience may harmonize with the above-suggested alteration of the silver sulfide particles during ripening, but in the absence of numerical data it can not be stressed.

Whether unreduced silver sulfide, in a particle of any size, can act as a nucleus in development,* in other words, can constitute latent fog appears, in view of these considerations, to be as yet unproved.

*Dr. Sheppard has pointed out that the fogging effect of simple excess of sulfiding sensitizer, without digestion, is certainly difficult of other interpretation.

Variations in the Threshold Speed of an Emulsion According to the Developer and Conditions of Development

While nothing less than the whole relation between density and exposure (or between density and the common logarithm of the exposure, this being graphically represented as the density curve, the so-called *characteristic curve*), can completely express the behavior of a given emulsion, for conciseness it is necessary to consider some part of the relation as representative of the whole.

In English-speaking countries it is customary to express the sensitiveness of photographic materials in terms derived from the intersection of the straight-line portion of the characteristic curve with the exposure axis. This method, which was introduced by Hurter and Driffeld,¹ expresses the speed in terms of the correct exposure portion of the density curve. In Germany, on the other hand, sensitiveness has usually been expressed in terms of the minimum exposure which is detectable. This minimum exposure corresponds, of course, to the extreme underexposure region of the density curve and is known as the "Schwellenwert," which may be translated "threshold value."

The threshold speed depends upon the time of development and the developer used, and it must be measured therefore under defined conditions, although it is remarkable that the German literature does not contain any very extensive study of the variation of threshold speed with the developer used. In investigations on the nature of the latent image from a chemical viewpoint, some criterion of the existence (or intensification, reduction, or destruction) of a latent image is essential, and it would seem that a judgment might well be based on the effects produced under such conditions of development that the minimum light-exposure is rendered evident; in astronomical, X-ray, and press photography the importance of the developability of faint light-impressions, that is, of extreme underexposure detail, is manifest. For this reason a study has been made of the effect of the developer and conditions of development on the threshold speed.

¹ F. Hurter and V. C. Driffeld: Photochemical Investigations and a New Method of Determination of the Sensitiveness of Photographic Plates, *J. Soc. Chem. Ind.* **9**: 455. 1890 (May 31).

For the purpose of this investigation the relative threshold speed of photographic emulsions is taken as being the ratio of the reciprocal of the respective minimum exposures which give on development a definitely perceptible image, the development being carried to the point at which the threshold speed is a maximum. As development is carried on, more and more of the image appears, fog develops, and finally the image appears to recede. In the measurements given here, development was carried on for the optimum time.

LITERATURE

The variation of the threshold speed of an emulsion according to the developer and conditions of development has been alluded to frequently, and there exist, particularly in the German literature of about 1900, some scattered experimental data. The general opinion at that time (Precht,² however, to the contrary) was that threshold speed does vary with the developer. As regards theory, von Hübl³ states that the capability of developing very feeble light-impressions corresponds to the chemical tension between the developer and silver bromide: he thus apparently considers that the threshold speed sequence of developers is identical with their reduction potential sequence.

The Lumière brothers and Seyewetz⁴ find that the threshold speed of Lumière Sigma plates is independent of the (chemical) developing solution used, except that "certain slow developers which exert a solvent action upon silver bromide, either by virtue of the developer itself (paraphenylene-diamine) or owing to the presence of potassium bromide or ammonium chloride, do not allow of the development of faint impressions of light to the same degree as do other developers." They tested the following developers, in the form of solutions prepared according to established formulas: diamidophenol, metoquinone, pyrogallie acid, paramidophenol, metol, hydroquinone, metol-hydroquinone, edinol, glycin, adurol, hydramine and paraphenylene-diamine.

Lüppo-Cramer⁵ finds, with high-speed plates (apparently only a single emulsion), that while a (chemical) developer such as metol-hydroquinone develops from 6 to 8 degrees of the

² J. Precht: *Phot. Korr.* **36**: 24. 1899 (Jan.).

³ A. von Hübl: *Die Entwicklung der photographischen Bromsilber-Gelatine-platten bei zweifelhaft richtiger Exposition* 13. 1901.

⁴ A. and L. Lumière and A. Seyewetz: On the Comparative Reducing Power of the Principal Developers. *Brit. J. Phot.* **56**: 627. 1909 (Aug. 13).

⁵ Lüppo-Cramer: Schwellenwert und physikalische Entwicklung. *Koll.-Zeits.* **29**: 314. 1921 (Dec.).

Eder-Hecht tablet, corresponding to $1/1.74$ to $1/2.09$ exposure, more than does glycine with potassium carbonate, the latter, although it gives an image of greater contrast, does not develop any lower exposure than is developed by the following treatment: Bathe in a solution containing 1 per cent of potassium iodide and 5 per cent of sodium sulfite crystals for 1.5 minutes, wash briefly, and develop in a solution of 5 g. of metol, 10 g. of citric acid, 2 g. of gum arabic and 250 c.c. of water, to which 10 c.c. of 10 per cent silver nitrate has been added before use.

EXPERIMENTAL

DETERMINATION OF RELATIVE THRESHOLD SPEED

The greater number of the organic developing agents, and also the silver nitrate and citric acid used, were the preparations of highest grade listed in the *Eastman Organic Chemicals* catalogue. The remaining chemicals were a high, or the highest grade of other manufacturers.

Fixation was in the regular acid-hardening bath, and care was taken not to leave the test-pieces in the bath for an unnecessary time.

A standard exposure was given, at a suitable distance, for 10 seconds, to a 250-watt 110-volt tungsten filament lamp run at 65 volts, through a Chapman-Jones "plate-tester" tablet the densities of the numbered fields of which had been measured, together with a Wratten No. 49C blue filter. The test-pieces after developing, fixing, washing, and drying, were inspected before an illuminator under constant optical conditions to determine the highest field number that could unquestionably be read in a definitely limited time (3 seconds). This threshold density (or density-difference with reference to fog) is possibly somewhat larger than that usually taken in estimations of the "Schwellenwert" or threshold speed. Judged by the repeatability of experiments by the writer, the uncertainty of an estimation of comparative threshold speed by this method does not exceed ± 15 per cent: Realizing that a total uncertainty of this magnitude arises in the preparation of the test-pieces, no attempt was made to increase the precision of the method of observation.

The length of the developed image scale does not usually remain at its maximum for as long as corresponds to a doubling of the time of immersion in the developer, yet, owing to the volume of work that would otherwise have been entailed, test-pieces were usually developed only for a series of times with a

factor of 2. Several other, probably less important, sources of uncertainty are: (1) The time elapsing between exposure and development was usually less than one hour, but it was not maintained constant, and it is possible that, under conditions ordinarily obtaining, a certain growth⁶ of latent image may continue during some hours after exposure. (2) Although the developing solutions were usually prepared only between a few minutes and a day before use it is known that in the cases of elon and hydroquinone the fogging action of the developer diminishes spontaneously during this interval, and its developing action for the light-exposure may accordingly be suspected of some variation. (3) The ratio of volume of developer solution to area of emulsion film was not constant, and, development being in trays, there were variations in the degree of agitation, and slight fluctuations of temperature during the longer times of development.

The results obtained by the procedure outlined above are probably not applicable to the conditions of practical photography, and it must not be taken therefore that the conditions of development which give the highest threshold speed are necessarily those most suitable for the development of underexposed negatives.* Fog and image often differ obviously in color, and in virtue of this alone without any density difference it may be possible to make a reading; and in any case no regard is given to the photographic (printing) value of the lowest image densities as compared with the adjacent fog. The readings obtained, however, correspond to useful sensitivity in the case of an X-ray plate or film when the "negative" is examined before the illuminator.

The behavior of Eastman Slow Lantern plates as regards apparent length of image scale on continued development of a standard exposure in an elon-hydroquinone developer is shown in Fig. 2. The developer was of the composition: elon,** 0.125; hydroquinone, 0.375; sodium carbonate (des.), 2.5; sodium sulfite (des.), 7.5; potassium bromide, 0.15; water, to 100. The temperature was 20° C. The observed fog density at 40 and 50 minutes (maximum of the curve) was 0.91 and 1.38, respectively.

It seems evident that the mere presence of a heavy uniform veil of fog is not the sole cause of the apparent disappearance of the lowest fields on protracted development. For if in contact with the face of a test-piece for the optimum time of development there is placed a sheet of film of uniform density

⁶ R. Colson: *La plaque photographique* 27. 1897.

*See, however, pp. 124-5.

**Elon is a metol-phenylmethanol sulfate manufactured by the Eastman Kodak Co. Metol is usually stated to be *p*-ethylamino-phenol sulfate but occasionally (especially in the older literature) *p*-methylanino-*m*-cresol sulfate.

so that the total fog density approximately equals that of a test-piece for a certain longer time of development, the threshold densities are still seen to differ in the same sense, whether the same arrangement or whether a brighter light is used for observation.

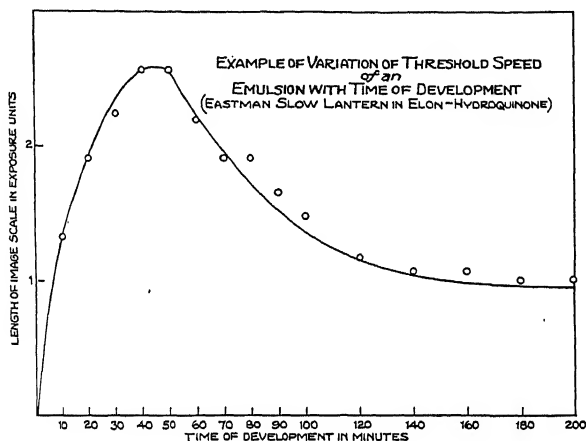


FIG. 2

Using plates of the same emulsion, a series of tests was carried out with a number of chemical and physical developing solutions. First, it was found in the cases of each of the three chemical developers, elon, hydroquinone, and pyrogallol, that the threshold speed of the emulsion did not vary appreciably (i)* when sodium hydroxide was used instead of sodium carbonate, (ii) when the sodium sulfite was reduced or omitted entirely, (iii) when the potassium bromide was omitted or increased to several times the usual content or (iv) when sodium sulfate was added to the solution so that it contained about 10 per cent of the anhydrous salt. Accordingly, solutions of other developing agents were generally made up only according to usual formulas,** such as those given in the *Brit. J. Phot. Almanac*. Taking as unity the (maximum, thresh-

*Lumières and Seyewetz varied the alkali, sulfite, and bromide concentrations in the developers they used (reference 4), and apparently found that the threshold speed of an emulsion then remains unchanged. The wording of the article is not absolutely clear as to their results.

**The use, in these experiments, of solutions with a definite molar content of the developing agent and of its constituents would doubtless have been somewhat preferable. It should be remarked, however, that in the present state of our knowledge regarding ionization of the developing agents, this would still not have placed the comparison on a strictly rational basis.

REACTIONS OF THE LATENT IMAGE

old) speed given by ferrous oxalate, the relative values found for chemical developers are as follows:

Elon, <i>p</i> -methylamino-phenol sulfate	4.
Diaminophenol	1.9
Paraminophenol	1.3
Hydroquinone	1.1
Ferrous oxalate	1.0
Hydroxylamine	1.0
Glycin, 1 : 4 C ₆ H ₄ (OH) (NHCH ₂ COOH)	0.9
Pyrogallol	0.7

A standard temperature of 20° C. was used in these (and all subsequent) cases of chemical development. It should be mentioned that the value obtained for diaminophenol with sulfite (as ordinarily used) was not changed when sodium carbonate was added. Rodinal (-Agfa) gave the same value as paraminophenol (with either sodium carbonate or sodium hydroxide). Hydroxylamine was used according to the formula: hydroxylamine hydrochloride, 0.5; potassium hydroxide, 0.7; water, to 100.

Physical development was carried out at a standard temperature of 18° C. As the effect of varying this was not tested, it seems possible that a somewhat lower temperature may be found preferable in future work. Physical development may be classed as (1) pre-fixation development, (2) development with simultaneous partial or complete fixation, or (3) post-fixation physical development.

For the case of pre-fixation physical development, and Eastman Slow Lantern plates as before, the speeds found, again relative to (chemical development in) ferrous oxalate as unity, are as follows:

Elon, preceded by iodide bath, and used with gum arabic according to Lüppo-Cramer's metol formula—see under "Literature."	0.4
Elon, omitting iodide bath, but otherwise used with gum arabic according to Lüppo-Cramer's metol formula.	0.2
Elon, with citric and acetic acids, according to Mees's modification of A. von Hübl's metol formula as cited by Lüppo-Cramer: metol, 2; citric acid, 10; water, to 100; with 3% of its volume of 10% silver nitrate solution added immediately before use. The modification is: elon, 1; citric acid, 1; acetic acid, 5; water, to 100; with 10% of its volume of 10% silver nitrate solution added immediately before use.	0.19
Hydroquinone, according to the formula: hydroquinone, 0.2; citric acid, 0.5; sodium acetate, 5; water, to 100; with 2% of its volume of 10% silver nitrate solution added immediately before use.	0.16
Elon, according to von Hübl's original metol formula as quoted in third entry of this table.	0.13

For two cases of physical development with simultaneous partial or complete fixation the speeds found are as follows:

Paraminophenol, according to the formula:⁷ water, 0.2
 100 c.c.; ammonium thiocyanate, 24 g.; silver nitrate, 4 g.;
 sodium sulfite cryst., 24 g.; sodium thiosulfate cryst., 24 g.;
 10% potassium bromide solution, 6 drops; with 6 c.c. of a
 solution obtained by diluting 2 c.c. of rodinal with 54 c.c.
 of water immediately before use.

Paraphenylenediamine, with sulfite, according to Schaum 0.19
 and Lang's modification⁸ of a formula of Lumière and
 Seyewetz's. The modification is: (A) sodium sulfite cryst.,
 18; silver nitrate, 0.75; water, to 100: (B) sodium sulfite
 cryst., 2; paraphenylenediamine, 2; water, to 100: 2 parts
 of A to be added to 1 part of B immediately before use.

For post-fixation physical development, fixation was carried out in a sodium sulfite solution containing about 18 grams of the anhydrous salt in each 100 c.c. In this way the uncertain and usually serious loss of latent image which occurs on fixing in hypo is probably largely obviated, but it must be admitted that nothing is directly known about the loss (if any) on fixing in sulfite. The plates were immersed in a relatively large volume of the solution, and if after several hours (at about 20° C.) the emulsion had not cleared, the solution was replaced by fresh, and this later, if necessary, by a third quantity. Washing was for one hour in running city water, and this was followed by development. These operations were conducted by yellow light, this precaution being considered desirable inasmuch as the emulsion is not entirely insensitive to light at any stage, except possibly between the washing and the development. The speeds found are as follows:

Elon, with gum arabic according to Lüppo-Cramer's 0.2
 metol formula (see "Literature").

Paraminophenol, with thiocyanate, *etc.*, according to 0.2
 the formula of first entry in preceding table.

Elon, according to von Hübl's formula (see third entry 0.19
 in table for pre-fixation physical development).

Paraphenylenediamine, with sulfite, according to Schaum 0.19
 and Lang (see second entry in table for simultaneous
 fixation and development).

Elon, with citric and acetic acids, according to Mees *0.17
 (see third entry in table for pre-fixation physical develop-
 ment).

Hydroquinone, formula as stated in fourth entry in table. *0.10
 for pre-fixation physical development.

⁷ R. Neuhaus: *Phot. Rund.* 12: 258. 1898.

⁸ K. Schaum and H. Lang: *Koll.-Zeits.* 28: 244. 1921 (June).

*These figures are probably too low. It was not certain that the maximum of the scale was found, and no plates of the same emulsion batch remained for further test.

On repeating several of the above described experiments with Eastman Slow Lantern plates of other emulsion batches, it was seen that while the developers either arranged themselves in the same series or could be so arranged if allowance were made for the experimental uncertainty, the scale was usually a less open one. For instance, instead of elon and hydroquinone standing in the ratio of approximately 4 to 1, this ratio was only 2 to 1 in the case of one other emulsion batch. Accordingly, it did not seem worth while to extend the experiments very far with the thought of constructing a developer series that might possess some real significance. Only a few somewhat scattered experiments, therefore, were carried out, first with the above-mentioned other batch of Slow Lantern plates and then with a few other plates and films and with one paper.

In order to see how the threshold speed of an emulsion may vary when the developing agent in an elon-hydroquinone developer changes progressively from pure elon to pure hydroquinone, Eastman Slow Lantern plates were developed, with the following results, hydroquinone being now taken as unity:

Elon, 0.5; Na ₂ CO ₃ , 2.5; Na ₂ SO ₃ , 7.5; water, to 100.	2.0
Elon, 0.375; hydroquinone, 0.125; Na ₂ CO ₃ , 2.5; Na ₂ SO ₃ , 7.5; water, to 100.	1.7
Elon, 0.25; hydroquinone, 0.25; Na ₂ CO ₃ , 2.5; Na ₂ SO ₃ , 7.5; water, to 100.	1.5
Elon, 0.125; hydroquinone, 0.375; Na ₂ CO ₃ , 2.5; Na ₂ SO ₃ , 7.5; water, to 100.	1.3
Hydroquinone, 0.5; Na ₂ CO ₃ , 2.5; Na ₂ SO ₃ , 7.5; water, to 100.	1

Again, to the pure elon developer was added, first, hydroquinone equal to, and, second, twice, the weight of the elon, with the results:

Elon, 0.5; Na ₂ CO ₃ , 2.5; Na ₂ SO ₃ , 7.5; water, to 100.	2.0
Elon, 0.5; hydroquinone, 0.5; Na ₂ CO ₃ , 2.5; Na ₂ SO ₃ , 7.5; water, to 100.	1.5
Elon, 0.5; hydroquinone, 1.0; Na ₂ CO ₃ , 2.5; Na ₂ SO ₃ , 7.5; water, to 100.	1.5

Test of other emulsions gave figures as follows for the ratio of the threshold speed found with pure elon to that found with pure hydroquinone:

Eastman Speedway plates	1.2 : 1
Eastman Process plates	2.4 : 1
Wratten & Wainwright Panchromatic plates	0.8 : 1
Eastman Super-Speed Portrait film	1.5 : 1
Eastman Commercial film	1.6 : 1
Velox paper No. 3	1.4 : 1

Other ratios found are:

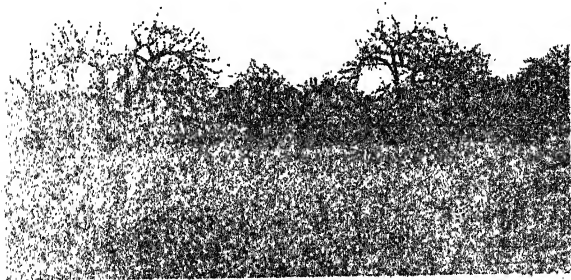
Eastman Speedway plates in Mees's physical developer before fixing and in ferrous oxalate.	0.16 : 1
Velox paper No. 2 in elon and in hydroquinone, observation being by reflected light.	1.6 : 1

A slight and in all cases somewhat doubtful diminution in the threshold speed of Slow Lantern plates was observed (i) when bromide (0.15 per cent KBr) was replaced by iodide (0.03 per cent) in either the pure elon or the pure hydroquinone developer used, (ii) when the pure elon developer was diluted with twice its volume of water, and (iii) when the pure elon developer was used at 5° C. instead of at 20° C.

A COMPARISON OF ELON WITH PYROGALLOL AS REGARDS THE PRINTING VALUE OF NEGATIVES DEVELOPED FROM AN UNDEREXPOSURE

The emulsion chosen for this test was one, Eastman Speedway, with which the visual threshold speed ratio for elon to pyrogallol was found so small (1.3 : 1) that it would not indicate with certainty, for a single determination, a real difference in the action of the two developers. Several determinations had been made, however, and the figure confirmed. The object of the test was to see whether a distinct photographic difference would be found in a case for which the visual difference is real but small, so that, in the event that it was, it could be inferred, that there is at least a probability of a similarity between the visual and the photographic series. Being also very fast, this particular emulsion seemed the more suitable for the test. A number of exposures were made in succession under conditions which would give extremely underexposed negatives. Alternately exposed plates were developed in elon, 0.5; Na₂CO₃, 2.5; Na₂SO₃, 7.5; water, to 100, for a series of times increasing with a factor of 1.5, at 20° C., until it was evident that the extreme under-exposure detail that had developed was now again gradually disappearing. The other alternate plates were developed according to the same plan but in pyrogallol, the "B. J. Non-staining Formula"⁹ being used. It was obvious on inspection before an illuminator that two or three of the elon-developed plates each showed more shadow detail than did the best pyrogallol-developed plate. Prints were now made on Velox paper No. 4 from each negative, the exposure being adjusted to suit a full development in an elon-hydroquinone developer. It was found that, with each series, the negative that showed the greatest shadow detail on inspection gave also the greatest detail in the print.

⁹ *Brit. J. Phot. Almanac* for 1927, p. 375.



PRINT ON NO. 4 VELOX FROM (1) ELON-
(2) PYROGALLOL-DEVELOPED, UNDER-EXPOSED EASTMAN
SPEEDWAY PLATE

THE THRESHOLD SPEED SERIES
AND THE ADSORPTION THEORY OF DEVELOPMENT

A possible dependence of the threshold speed series on differential adsorption of the developing agent was suggested by certain experiments of the writer's.¹⁰ Further work, however, failed to disclose any unquestionable evidence for adsorption of elon, hydroquinone or pyrogallol, from alkaline solution, by silver halide or gelatin;¹¹ and the suggestion that the threshold speed series may be the result of differences in the adsorbability of the developer to the silver halide appears, therefore, to be without foundation in fact.

THE THRESHOLD SPEED SERIES AND A
POSSIBLE DIFFERENTIAL DESTROYING ACTION
OF THE DEVELOPERS ON THE LATENT IMAGE

A possibility to be considered is that the developers low in the series may while developing a part of the latent image destroy the remainder, or, supposing that all developers destroy some of the latent image, that the developers low in the series may destroy a greater fraction of it than do those higher. If after developing a plate in pyrogallol for the time required to give the maximum length of image scale, it should be possible, by continuing development in an elon solution, to develop additional image at the bottom of the scale, it would seem very probable that the failure of pyrogallol to develop as low an exposure as does elon is not due to destruction of the low-exposure latent image by the pyrogallol. Using Eastman Process plates, and developing to the optimum in either pyrogallol or hydroquinone, then washing for 15 minutes, and developing for a certain time in elon, it is indeed found that additional image appears. When, however, by varying the times of immersion, the new maximum is obtained, it is seen that this is intermediate between the pyrogallol or hydroquinone and the true elon maximum—and never equal to the latter. By developing in pyrogallol or hydroquinone for one-half the respective times for the maximum scale, and then, as before, washing and continuing in elon, the new maximum is found greater than before but still not quite equal to the true elon maximum. Owing to the complicating influence of fog, it is not possible to draw any perfectly definite conclusion from these experiments, but they favor the view that the threshold series owes

¹⁰ *Sci. ind. phot.* **6M**: 37. 1926 (July).

¹¹ *Sci. ind. phot.* **7M**: 6-7. 1927 (Jan.).

its existence to differences in the low-exposure developing ability, and not to a differential destruction of latent image by the lower members of the series.

ARE THERE CERTAIN EMULSIONS FOR WHICH
THE THRESHOLD SPEED FOR CHEMICAL DEVELOPMENT IS INDEPENDENT OF THE DEVELOPER?

In the experiments described, all the emulsions used, with the exception of Wratten & Wainwright Panchromatic, showed a developer variation of threshold speed. The value for the ratio of elon to hydroquinone with Eastman Speedway (1.2 : 1) had been confirmed and is probably real. W. & W. Panchromatic gave 0.8 : 1 for this ratio in a single determination. Instead of repeating this, single determinations with two other emulsions of a similar type, Eastman 36 and Eastman 40, have been made, with the results 1 : 1 and 1.3 : 1, respectively. These scanty data suggest that there is a type of high-speed emulsion for which the threshold speed series does not obtain but for which the threshold speed is independent of the developer.

INFLUENCE OF THE PRE-DEVELOPMENT CONDITIONS
ON THE THRESHOLD SPEED OF AN EMULSION FOR
POST-FIXATION PHYSICAL DEVELOPMENT

In the experiments on post-fixation physical development that have been described the conditions as to fixing and washing were maintained constant, and the plate, without drying, was placed in the physical developer and developed for various times in a geometrical progression with a factor not greater than 2 so that a value might be found for the maximum image scale, that is, for the relative threshold speed, for the particular developer. In new experiments, the developer was not varied, but only the conditions of fixation and washing. As explained later, these experiments, after sodium sulfite solution had been used for fixation, were prematurely discontinued.

The sodium sulfite used was Merck's "reagent" crystals. These are presumably and apparently highly pure, apart from the changes (dehydration and oxidation) that take place on keeping in the ordinary 1 lb. cork-stoppered bottles. Judged by the concentration of its solution that most rapidly fixes an emulsion, its sulfite content might be assumed to be somewhat higher, allowing for water of crystallization, than that of the

high purity dry sulfite previously used. It was taken, therefore, as containing 50 per cent sodium sulfite.

Solutions of, respectively, 12.5, 15, 17.5, and 20 per cent Na_2SO_3 were compared as regards the rate of fixing of Eastman Slow Lantern plates and also as regards the threshold speed for a definite, not necessarily the optimum, time of development. The solution was changed, as before, every two hours, until the emulsion cleared. Development was for 25 minutes, at 18°C. , in the Mees developer: elon, 1 g.; citric acid, 1 g.; acetic acid, 5 c.c.; water, to 100 c.c.; with 10 c.c. of 10% silver nitrate added immediately before use. It was observed that the sulfite solutions of middle concentration fixed faster than either the 12.5 or the 20 per cent solution, but it could not be decided without further tests whether the 15 or the 17.5 per cent solution was the faster. A similar result was obtained for the speed—the value 0.25 (relative to maximum ferrous oxalate speed as 1) was obtained for the 15 and 17.5 per cent solutions, a slightly lower value for the 12.5 per cent, and 0.20 for the 20 per cent solution. This speed variation, however, is within the experimental uncertainty, which may still be taken, in the absence of more definite knowledge, as ± 15 per cent.

The washing between fixing and developing had been for one hour. It was now varied, no washing, and washing for 20 minutes, 1 hour, 3 hours, and 18 hours, in running city water, by a yellow safelight or in darkness, being given, when the speeds observed were respectively 0.17, 0.25, 0.25, 0.38, and 0.38.

After clearing in sulfite (two successive baths for about 2 hours each), an exposed plate was transferred to a third bath of 15 per cent Na_2SO_3 and left overnight, then washed for 1 hour, and developed for 25 minutes as usual. The threshold speed observed was 0.17.

An experiment, with normal procedure except that the plate was allowed to dry between washing and developing, gave 0.38.

In the above-mentioned experiments, a constant time of development (25 minutes) had been given, owing to the tediousness of developing for a series of times in order to obtain a value for the maximum speed in each case, and also owing to the cost of the pure sodium sulfite required. Using the normal procedure—fixing in successive 2-hour baths of 15 per cent Na_2SO_3 until cleared, washing for one hour in running city water, and immediately developing—the time in the developer was now varied, 16, 24, 36, and 54 minutes being given:

the same, unexpectedly high threshold speed of 0.6 was obtained in each case.

All these results are rather puzzling, and seem to point to the existence of some neglected experimental condition of unsuspected importance.

Occasionally, not only in the above-described experiments, but also in previous ones on development after fixation in sulfite, a faint visible image was evident after fixing and before development. Contamination of the (enameled steel) tray with a trace of ferrous oxalate or other as-yet unoxidized developer seemed, in view of the length of the immersion given in the sulfite solution, a possibility in explanation of the phenomenon. Inasmuch as development by a solution of sodium sulfite with carbonate has been described,¹² it seemed possible that slight variations in the alkalinity of the sodium sulfite itself might account for the erratic nature of the observations. Addition of sodium carbonate equal to 1 and 3 per cent Na_2CO_3 to the sulfite bath resulted, however, only in a moderate slowing of fixation, without any image being visible before immersion in the physical developer: the relative speeds, for 25 minutes' development, were 0.38 for 1 per cent, and 0.32 for 3 per cent, addition of Na_2CO_3 .

Further investigation of post-fixation physical development must be deferred for the present. There is a suggestion that in all cases where post-fixation development is observed there may occur a slight development (growth of latent image nuclei) *during fixation*. Conclusions regarding the complexity of the latent image, the reasons for the threshold series of developers, and such matters, cannot therefore, in view of this possibility, be based with any degree of confidence on the phenomena of post-fixation physical development.

RECESSION OF THE IMAGE SCALE ON CONTINUED DEVELOPMENT

An effect which is striking in its generality and which, as far as the writer is aware, has never been exactly described and discussed in the literature, is what may be called the recession of the developed image scale on protracted development. In the figure illustrating the variation of threshold speed of an emulsion with development (p. 120), it is evident that the speed is reduced to about two-fifths of the maximum for the particular developer by continuing development for 155 minutes after the maximum has been reached. As viewed

¹² J. M. Eder: *Ausf. Handb. Phot.* III, 835. 1903. The reference is to work by K. Schaum and W. Braun.

before an illuminator, the lower fields of a tablet exposure, after extending themselves downward, with but little hesitation turn and recede upward: in other words, with continued development new fields first appear, the image is briefly stationary, and fields then disappear one by one from the bottom of the scale. Every emulsion and every developer (chemical, or pre-fixation or post-fixation physical) appears to show this effect, although the time required for the developed image to commence to recede may vary, according to the emulsion and developer, from less than 10 minutes to 5 hours or longer. The (continuously increasing) development fog may at the point of maximum length of image scale be as little as 0.04 for one developer and as much as 1.5 for another even in the case of one and the same emulsion (Eastman Slow Lantern). With very protracted development, in the case of certain emulsions, some or all of the lower image fields that have disappeared from observation reappear in a reversed condition, that is, having a density lower than that of the adjacent fog, which has now usually increased to a high value.

DISCUSSION OF THE RESULTS

The phenomena which have been described appear to indicate the existence of two effects. The first of these is the falling of developers into a fairly well defined series according to the minimum exposure that suffices for a clearly perceptible density or density-difference. The second is the gradual disappearance, in some cases followed by reversal, of the lowest exposure fields, or of the extreme under-exposure details of a camera exposure, on prolonging development. It is not known how far these effects are interdependent, but it seems certain that the first, the observed threshold series, must in some degree be complicated by the second, the recession of the image scale. The latter effect may perhaps, for convenience of classification, be considered as the preliminary stage of one kind of *pseudo-solarization*, the name given by Liesegang¹³ to a partial or complete reversal that might make its appearance in the development of a normal exposure. Reversal of extreme under-exposures on protracted development with an ordinary sulfite-containing developer has long been known. Lüppo-Cramer^{14, 15}

¹³ R. E. Liesegang: *Phot. Korr.* 32: 536. 1895 (Nov.). If the plate became light-struck during development, or if the emulsion contained a soluble silver salt, or the developer a notable silver halide solvent such as paraphenylenediamine, ammonia, thiocarbamide, or hypo the reversal which occurred under these conditions was called *pseudo-solarization*.

¹⁴ *Photographische Probleme* 190. 1907.

¹⁵ Lüppo-Cramer: *Dichroitischer Schleier und Pseudo-solarisation. Phot. Ind.* 18: 37. 1920 (Jan. 14).

mentions it, and considers that the effect is to be explained by the greater covering power of silver in the form of fog as compared with the silver produced by development of a feeble light-exposure, such a difference in covering power having, he states, been recognized by Liesegang. Some doubt is cast upon this explanation by the fact that, in the writer's experiments, it is found that the fog* at the point of maximum image scale may vary very greatly according to the developer. That the fog produced by the protracted development of an unexposed area of an emulsion film may have a covering power not only not greater than that of a similarly developed, fully exposed area but actually only about one-fifth as great, is shown by the work of Sheppard and Ballard.¹⁶ It seems probable that if silver values were used instead of visual densities in plotting the relation between threshold speed and time of development, the curve on passing the maximum would descend more steeply, than it does, that is, the recession effect would be accentuated rather than removed.

Sheppard¹⁶ has pointed out that, taking into account his observations, and the work of Davidson and of Wilsey and Pritchard, it now appears that "the covering power of the silver deposit is determined not only by original grain-size, but also by number of sensitizing nuclei and their conversion to development centers."

The second effect, the falling of chemical developers into a more or less definite sequence, as seen with Eastman Slow Lantern plates, according to the relative threshold speed at the optimum time of development, is interesting. It is a question whether this sequence, which appears to hold for the greater number of emulsions, is actually, as suggested by von Hübl,³ the reduction potential sequence. The chemical reduction potential depends on the nature of the reducing substance and on its concentration in the solution. The variation with concentration is, however, quite small, and need scarcely be considered when discussing developing solutions of ordinary practical formulas. The actual reducing substance in chemical developers is usually an anion, but it may be an undissociated molecule; and it is usually a cation in physical developers. The case of elon (*p*-methylamino-phenol) may be taken as an illustration. By virtue of its hydroxy- group it yields, in a sufficiently alkaline solution, an anion, and, similarly, in an acid solution, by virtue of its methylamino- group, a cation;

*Fog is considered as a whole, measured by its opacity or by the silver composing it, and the question of its possibly composite origin and physical character is disregarded in this chapter.

¹⁶ S. E. Sheppard: The Covering Power of Photographic Silver Deposits. *Phot. J.* 66: 470. 1926 (Sept.).

in nearly neutral solutions it may exist largely as the undissociated molecule. The *p*-methylamino-phenol anion has a greater reduction potential than the cation, while the molecule is intermediate. A test of the (nearly neutral) solution: elon, 0.5; Na₂SO₃, 7.5; water, to 100: gave with Slow Lantern plates a threshold speed of 0.9 relative to ferrous oxalate as 1. It thus appears from the data that elon has the highest position in the threshold speed series when strongly or moderately alkaline, an intermediate one in nearly neutral solution, and the lowest position (for physical development) when strongly acid. These facts, therefore, as far as they go, seem to favor the suggestion that the threshold speed series may be identical with the reduction potential series. But it is found that the addition of either hydroquinone or pyrogallol to a pure elon developer lowers the maximum threshold speed of a slow emulsion, and this, without special assumptions, is not in harmony with the suggestion.

A TENTATIVE VIEW OF THE ORIGIN OF THE THRESHOLD SPEED SERIES

The writer supposes first that the medium surrounding the silver halide grain is such as permits diffusion but does not permit convection. There will then, in development, be established a zone of chemical reaction. Very close to the grain, within the inner surface of the reaction zone, silver ions (cations) will be in excess and the system will be an oxidizing system, while outside the outer surface of the reaction zone the reducing ions (usually anions) of the developing agent will be in excess and the system will be a reducing system. On diffusing through the reaction zone toward its inner surface the concentration of the reducing ion will diminish and the concentration of the reaction products will at first increase but then rather tend to remain constant, so that the main factor which determines equilibrium at the inner surface will be the lowering in concentration of the reducing ion to the point at which, in presence of the reaction products, it is no longer able to reduce silver cations. Comparing two different reducing ions, it would seem probable that the one which is able to continue reducing silver cations the longer, in presence of the reaction products, when its own concentration is continuously diminished, is the one which will penetrate the farther toward, and establish its inner reaction zone surface the nearer to, the silver halide grain.

The writer has supposed (*Brit. J. Phot.* **72**: 494. 1925) that the latent light-image in its most characteristic form is a

silver atom at rest. For ordinary chemical development this silver atom (not ion) will be on or in the surface of a particle of silver halide. Such a silver atom may be able to capture, as it were, another silver atom that moves into its immediate neighborhood, but is not, in general, able to capture an aggregate of silver atoms.

Now the nearest points to the latent image at which silver atoms are formed are on the inner surface of the reaction zone. These silver atoms are in motion and will diffuse in all directions in the medium, but at the same time, on collision, will tend to coalesce. The nearer to the low-exposure image they are formed, the greater will be their chance of reaching it unaggregated and so susceptible of capture by the silver-atom* nucleus. Thus elon, whose anion is able, in extremely low concentration, to discharge a silver cation may be able to develop the latent image of lower light-exposures than can be developed by hydroquinone or pyrogallol, whose anions act only in higher concentration.

The suggestion is now offered that the threshold speed series may, as regards sequence, be the inverse of the K series, K being the equilibrium constant for the (instantaneously) reversible reaction, $\text{Ag}^+ + \text{R}^- \rightleftharpoons \text{Ag} + \text{R}$, where R^- is the reducing ion and R its immediate oxidation product.

SUMMARY AND CONCLUSIONS

For every emulsion and developer, at a given temperature, there is an optimum development time at which the minimum light-exposure is rendered just visible, that is, at which the threshold (Schwellenwert) speed of the emulsion is a maximum. For a given, slow emulsion, this maximum threshold speed is primarily dependent on the actual reducing substance(s) in the developing solution, and is scarcely affected by variation in the concentration of the sulfite, bromide, and other constituents. The various ordinary (chemical) developing agents form a series, of which elon (*p*-methylamino-phenol) occupies the highest position, and pyrogallol the lowest. This series bears some resemblance to the Watkins-factor series, but there is this marked difference, that the former is independent of the bromide concentration. Its resemblance to the reduction

*The more generally accepted view that the minimum latent image nucleus contains about 300 silver atoms is not equally helpful in this explanation, for it is difficult to imagine that many silver particles of this order of atomic aggregation are able to reach the silver halide grain surface by diffusion through the medium. If it be admitted that all moving silver particles that reach the surface are smaller than a latent image nucleus, then, apparently, on this view, all these particles would be susceptible of fixation, and no differentially greater development should be seen with developers that are able even in extremely low concentration to reduce silver cations and so allow unaggregated, or relatively slightly aggregated, silver atoms to reach the grain surface.

potential series is probably closer. The threshold speed series is a continuous one, from alkaline chemical developing solutions, in which the actual reducing substance is an anion, to nearly neutral or acid silver-containing physical ones, in which the reducing substance is a cation. For emulsions faster than Process, the same sequence probably holds, but the difference between individual chemical developers is usually less and is often only of the same order as the experimental uncertainty.

In the case of a certain fast emulsion it has been shown that, when the optimum time of development is approximately known, an appreciably greater amount of printing detail may be obtained with a pure elon developer than with one of pyrogallol, from an extreme under-exposure. It is considered probable that the photographic threshold series is parallel to the visual threshold series of developers, and that the use of developers high in the series would be found advantageous for the development of negatives from under-exposures, not only with all slower emulsions, but also with the greater number of high-speed emulsions.

An examination of the possibility that the threshold speed series might be the result of differences in the degree of adsorption of the developer to the silver halide has disclosed no evidence for any adsorption of elon, hydroquinone, or pyrogallol from alkaline solution, by silver halide or gelatin.

Erratic results obtained in experiments on the variation of threshold speed with fixing conditions in post-(sulfite-)fixation physical development are probably connected with an incipient developing-out in the sulfite solution. It is concluded that the phenomena of development after fixation cannot in any case be accepted as having any necessary significance in such questions as the origin of the threshold series and the complexity of the latent image.

Beyond the optimum time of development, the developed image scale begins to recede, in other words, the lowest exposure fields of a tablet exposure begin to disappear for visual observation such as before an illuminator, one by one, or the extreme shadow details of a camera exposure are lost, little by little. This effect is seen with every emulsion and every (chemical or physical) developer. It is scarcely appropriate to say that the image becomes lost or buried in fog, because the effect persists on increasing the illumination and with certain emulsions and developers there is a transition, of the lowest exposure fields, through disappearance to reversal.

The threshold speed series of developers is connected, it is suggested, with differences in the closeness of approach of the

chemical reaction zone to the silver halide surface. With a pure elon developer free silver atoms are produced nearer to the latent image than with pure pyrogallol, and the chance is greater that they may reach it before coalescence, and so satisfy a condition for the growth of the (supposedly atomic) nucleus produced by the lowest developable light-exposures.

CHAPTER VII

The Latent Image or Latent Fog Produced by Certain Imperfectly Understood Actions-at-a-Distance (Russell Effect)

This chapter is mainly a review of the Russell, Colson-Russell, or Vogel-Colson-Russell effect, and is preliminary to an experimental comparison of the latent image or fog produced by this effect and that produced by light. The effect may be described, although not very satisfactorily, as a "quasi-photographic action-at-a-distance not known to be due to radiant energy of any frequency, to electrons, or to corpuscles such as alpha-particles."

The effect is of practical importance in connection with the slow deterioration, on storage, of most photographic sensitive materials through the spontaneous growth of latent fog.

It will be clear that fogging effects produced by the actual contact of solids, liquids, or solutions with the emulsion film are not considered in this review.

LITERATURE

In two articles on the appearance of black margins in dry plates, Vogel¹ traces the principal cause for the edge-fog observed on developing stored silver halide gelatin plates, to the black wrapping paper, and, further, to some impurity in the paper as used. He finds that pure paper, such as Swedish filter paper, does not produce edge-fog. Vogel's conclusion, that "jedenfalls sind es Gase, welche die Zersetzung verursachen," seems to entitle him to a place with Colson and Russell in the naming of this effect.

In "a contribution to the study of edge-fog on gelatin dry plates" Hertzka² makes some not very happy suggestions based on his casual observations, as to the causes of edge-fog.

Using Lumière Blue Band plates, and metol developer, Colson³ observes a latent fogging action from zinc, magnesium, and cadmium, and attributes this effect to traces of vapor of these metals.

¹ E. Vogel, jun.: Die Ursache der Entstehung schwarzer Ränder bei Trockenplatten. *Phot. Mitt.* 26: 9. 126. 1889 (Apr. and Aug.). Also in *Vogel's Handbuch* I. 314. 1890.

² A. Hertzka: Ein Beitrag zum Studium des Randschleiers bei Gelatinetrockenplatten. *Phot. Mitt.* 33: 70. 1896 (June).

³ R. Colson: Action du Zinc sur la Plaque Photographique. *Bull. soc. franç. phot.* 12: 338. 1896 (July).

Pellat,⁴ in a note on vaporization of metals at the ordinary temperature, relates that his experiments, four years before, showed that steel, in the form of a magnetized bar, has an action (in 2 weeks to several months) on a photographic plate even when separated from it by a sheet of cardboard.

Colson⁵ finds that an electric charge increases the latent fogging activity of zinc; and that the sensitivity of different plates to the action of zinc varies in the same sense as their sensitivity to light.

In his first paper "on the action exerted by certain metals and other substances on a photographic plate," Russell⁶ offers no definite explanation of the described effects.

In an account of "further experiments on the action exerted by certain metals and other bodies on a photographic plate," Russell⁷ states that a similar activity is found for polished metals of relatively high potential, and also for pure terpenes and resin-containing substances, and remarks: "Now, the important property belonging to all these bodies is their reducing or oxygen-absorbing power, hence the conclusion that it is this property which enables them to act on the photographic plate."

Tucker⁸ writes: "An Ilford Ordinary plate, which I had kept in its box unopened for five years, was exposed recently upon a poorly-lighted subject; upon development I found, instead of my subject, the matter of the advertisement that was upon the outside wrapper. This came up strong and quickly, but nothing was seen of the subject upon which the plate had been exposed in the camera.

"The image was a positive, and the large-type word 'Ilford' was very prominent.

"So it would appear that the sensitized plate had been acted upon by the printer's ink, through the lid of the box and three wrappers of paper, two of which were brown."

W. J. Russell comments: "A very interesting result. The picture no doubt arose from the printer's ink, and it shows what great lengths of time will do. The plate must have been face upwards."

⁴ H. Pellat: *J. Chem. Soc. (Abst.)* **70**: ii. 601. 1896 (Nov.). From *Comp. rend.* **123**: 104. 1896.

⁵ R. Colson: Action du Zinc et d'Autres Métaux sur la Plaque Photographique. *Bull. soc. franç. phot.* **13**: 316. 1897 (June).

⁶ W. J. Russell: On the Action Exerted by Certain Metals and Other Substances on a Photographic Plate. *Brit. J. Phot.* **44**: 437. 490. 1897 (July 9 and 30).

⁷ W. J. Russell: Further Experiments on the Action Exerted by Certain Metals and Other Bodies on a Photographic Plate. *Brit. J. Phot.* **45**: 246. 1898 (Apr. 22).

⁸ W. T. Tucker: *Nature* **58**: 32. 1898 (May 12).

In an article on the action of certain metals and organic substances on the photographic plate, Eder⁹ gives an account of Russell's communication as it appeared in the *Journal of the Camera Club*, and reviews the subject to date.

Repeating Russell's experiments with oil of turpentine, Sperber¹⁰ concludes that this substance emits an especially active dark-radiation.

In a paper on the optical properties of residual invisible luminescence, Le Bon¹¹ concludes from his experiments with calcium sulfide, "(1) qu'il y a identité complète entre la lumière solaire et la lumière absolument invisible émise par les corps qui ont vu la lumière du jour pendant un instant: (2) que cette luminescence résiduelle se conserve pendant fort longtemps, mais finit par se dissiper entièrement." (Compare the phenomenon of "photechy," ref. 21.)

In a paper on hydrogen peroxide as the active agent in producing pictures on a photographic plate in the dark, Russell¹² concludes from his previous work and further experiments now described, "that hydrogen peroxide is the agent which directly or indirectly causes the changes in the photographic plate."

Vincent¹³ finds that substances such as india-rubber, previously inactive, are capable of fogging a photographic plate after brief contact with ozonized air (itself inactive), and that the effect is obtained through paper or gelatin, but not through metals, glass, or quartz.

In an article on "the true cause of dark plate edges, and their prevention," Krone¹⁴ states that daylight penetrating by degrees through the packing is the solution of the question. It is the writer's experience that typical latent edge-fog that increases with time is *not* usually due to light-leakage, but usually to an action of the wrapping paper.

Von Lengyel¹⁵ finds that hydrogen, ethylene, methane, and carbon monoxide, in contact with a silver bromide gelatin plate, produce latent fog, but oxygen, nitrogen, carbon dioxide, and nitric oxide do not. He finds that zinc acts strongly in

⁹ J. M. Eder: Die Wirkung von gewissen Metallen und organischen Substanzen auf photographische Platten. *Eder's Jahrbuch* **13**: 9. 1899.

¹⁰ J. Sperber: *Eder's Jahrbuch* **13**: 501. 1899. From *Chem.-Ztg.* **22**: 661. Also, *Brit. J. Phot.* **46**: 71.

¹¹ G. le Bon: *Comp. rend.* **128**: 174. 1899.

¹² W. J. Russell: On Hydrogen Peroxide as the Active Agent in Producing Pictures on a Photographic Plate in the Dark. *Brit. J. Phot.* **46**: 185. 1899 (March 24).

¹³ J. H. Vincent: On Some Photographic Phenomena Connected with the Colson-Russell Effect. *Brit. J. Phot.* **46**: 422. 1899 (July 7). From *Chem. News*.

¹⁴ H. Krone: Die wahre Ursache der dunkeln Plattenränder und deren Verhütung. *Eder's Jahrbuch* **14**: 112. 1900.

¹⁵ B. von Lengyel: *Eder's Jahrbuch* **14**: 531. 1900. From *Wied. Annal.* **66**: 1162.

moist carbon dioxide and air, and supposes this results from a slight liberation of hydrogen.

Colson¹⁶ gives a comprehensive historical account of the influence of gases and vapors on photographic films.

In an article on "picture making in the dark," Wilbert¹⁷ alludes to substances not visibly phosphorescent, such as plaster of paris, white sugar, and glazed white paper, which after exposure to bright light, possess the property, although not visibly phosphorescent, of fogging a photographic emulsion in the dark. From the viewpoint of photographic printing, Wilbert also considers the latent fogging action of (polished) metals such as zinc, and of organic compounds of the nature of terpenes.

Liesegang¹⁸ describes the experiment of partly covering a silver chloride gelatin emulsion-coated glass plate with tin foil, wrapping three times in black paper, and arranging, with a number of ordinary phosphorus matches at a distance of two centimeters from the emulsion film, in a light-tight box. After two hours, blackening was clearly shown on the portion of the plate that was not covered with the tin foil. This effect is ascribed to the action of phosphorus vapors. The blackening observed was probably a development, not a "print-out" effect, but in the original this is not entirely clear.

In a paper "on the nature of the action of hydrogen peroxide on the photographic plate in Russell's experiments," Lüppo-Cramer¹⁹ states that hydrogen peroxide does not produce fog on collodion emulsion plates. Increasing concentrations of either hydrogen peroxide or ammonium persulfate solutions may give reversal with gelatin emulsion plates.

With hydrogen peroxide and a near-by photographic film, Grätz²⁰ finds a latent fogging effect which passes through thin metal films and which is not blown aside by a current of air. It should be remarked that these results were, later, not confirmed by Dombrowsky (Dissertation: 1908).

In a paper "on striking phenomena recognizable by the photographic plate," Blaas and Czermak²¹ term the increase or creation of photographic activity by pre-exposure to light,

¹⁶ R. Colson: Revue des Actions à Distances Capables d'Influencer les Couches Photographiques. *Bull. soc. franç. phot.* **16**: 481. 1900.

¹⁷ M. I. Wilbert: Picture-Making in the Dark. *J. Frank. Inst.* **150**: 388. 1900 (Nov.).

¹⁸ R. E. Liesegang: Phosphorographie. *Archiv wiss. Phot.* **2**: 239. 1900 (Dec.). From *Phot. Wochenbl.* **26**: 289.

¹⁹ Lüppo-Cramer: Ueber die Wirkungsart des Wasserstoffsperoxydes auf die photographische Platte bei den Russell'schen Versuchen. *Phot. Korr.* **39**: 563. 1902 (Oct.).

²⁰ L. Grätz: *Z. physik. Chem.* **47**: 497. 1904 (March 15). From *Drudes Ann.* **9**: 1100.

²¹ J. Blaas and P. Czermak: Über auffallende, durch die photographische Platte erkennbare Erscheinungen. *Physik. Z.* **5**: 363. 1904 (July 1).

as shown by paper, leather, *etc.*, and by zinc, *photechy* (*Photechie*). They conclude that photechy is connected with an occlusion of ozone (not hydrogen peroxide) which acts on a photographic plate in consequence of the emission of a diffuse radiation of the nature of blue light. It should be remarked that Blaas and Czermak were apparently unaware of the work of Niepce de Saint-Victor (1857), Colson, and Russell.

Schaum and Braun²² find that ozonized air has first a latent fogging and then a "printing-out" effect on medium-free silver bromide or a silver bromide gelatin plate. They observe also a powerful latent fogging action on gelatin emulsion plates by the vapor of hydrogen peroxide, sodium peroxide solution, ammonium persulfate solution, oil of turpentine, oil of lavender, ethyl ether, and methyl alcohol. The vapors of pure ethyl alcohol and acetone had no effect.

In a paper "on the action of wood on a photographic plate in the dark," Russell²³ gives an account, finely illustrated, of his further experiments on the fogging action of English and other woods in contact with, or supported above, a photographic plate. Activity is correlated with the presence of resins. It is greatly increased by a pre-exposure to white or blue light.

In a lecture, Grätz²⁴ demonstrates the then known peculiarities in the latent fogging action of hydrogen peroxide vapor, and remarks that he has observed no fogging action in the case of dry or moist ozone.

Unaware of Russell's publications of 1897-9, Czermak²⁵ gives an account of work by J. Blaas and himself.

Schaum²⁶ remarks that the activity of unisolated metals has been explained by the radioactivity theory (Crookes, and later Bogolawjenski), the electrolytic theory (Streintz), the hydrogen theory (von Lengyel), the hydrogen peroxide theory (Russell), and the metal vapor theory (Colson); and that the activity of isolated metals, resins, *etc.*, (photechy), has been principally explained by the formation of ozone on the surface and its partial retention (Blaas and Czermak).

²² K. Schaum and W. Braun: Chemische Wirkungen auf photographische Schichten. *Z. wiss. Phot.* 2: 285. 1904.

²³ W. J. Russell: On the Action of Wood on a Photographic Plate in the Dark. *Phil. Trans.* B197: 281. 1904 (Oct. 15).

²⁴ L. Grätz: Über die strahlungsartigen Erscheinungen des Wasserstoffsperoxyds. *Physikal. Z.* 5: 688. 1904 (Nov. 1).

²⁵ P. Czermak: Wirkung verschiedener Substanzen auf photographische Platten. *Eder's Jahrbuch* 19: 41. 1905.

²⁶ K. Schaum: Die photographische Wirksamkeit von Metallen und photechischen Stoffen. *Z. wiss. Phot.* 2: 427. 1905 (Jan.).

Kahlbaum and Steffens²⁷ name the latent fogging distance-action of aluminium, zinc, and other metals, *actinautography*; and attribute the effect to an emanation subject to gravity.

Kahlbaum²⁸ finds that the action of a number of metals laid without direct contact between two facing photographic films is as if a heavy fogging emanation were emitted; the effects are seen most distinctly in warm, moist air.

Schaum²⁹ finds that plates differ greatly in their sensitivity towards ozone; non-orthochromatic Agfa and Perutz plates, for example, being very sensitive. Grätz's failure to observe an effect is due to his use of an ozone-insensitive brand of plate.

Struthers and Marsh³⁰ find that pure mercuric chloride, either before or after purification, fogs a plate which is supported above it; but that redistilled mercury metal is quite inactive. Later, Dombrowsky was unable to confirm the fogging action of the vapor or radiation from pure dry mercuric chloride (Dissertation: 1908).

Streintz and Strohschneider³¹ make experiments from which they conclude that the higher the position of the metal in the potential series, the more pronounced the latent fogging action of its oxide-free surface is on a photographic film.

In an account of "investigations on the origin of the edge-fog of silver bromide gelatin dry plates," Homolka³² describes experiments from which he concludes that edge-fog is to be attributed to the result of a migration of the small amount of soluble bromide from the edges towards the center of the plate during the original drying of the emulsion. By edge-fog, however, Homolka means what is perhaps more correctly termed edge-sensitivity, the abnormal sensitivity that is usually found along the original coating edges of a recently coated plate, and seen either on flashing and developing, or after ordinary storage, wrapped in paper, as a mixed effect, on mere development.

Gaedicke³³ explains edge-fog as due to formaldehyde vapor

²⁷ G. W. A. Kahlbaum and M. Steffens: Über die spontane Einwirkung von Metallen auf die empfindliche Schicht photographischer Platten bei Vermeidung jedes direkten Kontaktes. *Physik. Z.* **6**: 53. 1905 (Jan. 15).

²⁸ G. W. A. Kahlbaum: *Chem. Zentralbl.* **76**: I. 323-4. 1905 (Feb. 1).

²⁹ K. Schaum: Über die photographische Wirksamkeit des Ozons. *Physik. Z.* **6**: 73. 1905 (Feb. 1).

³⁰ R. de J. F. Struthers and J. E. Marsh: Photographic Radiation of Some Mercuric Compounds. *J. Chem. Soc.* **87**: 377. 1905.

³¹ F. Streintz and O. Strohschneider: Versuche über Metallstrahlung. *Ann. Physik* **18**: 198. 1905 (Oct. 15).

³² B. Homolka: Untersuchungen über die Entstehung des Randschleiers der Bromsilber-gelatine-Trockenplatten. *Phot. Korrr.* **42**: 550. 1905 (Dec.).

³³ Gaedicke: *Eder's Jahrbuch* **21**: 481. 1907.

which is generally present in the atmosphere of large cities, and which attacks dry gelatin less readily than moist. The first drying portions of the plate, the edges, are thus less exposed to the tanning action of the atmospheric formaldehyde, and darken in a developer more readily than do the central portions of the plate.

Campbell³⁴ observes a feeble photographic effect in several weeks, apparently due to emission of β -rays, from potassium salts as compared with a sodium salt. It should be remarked that potassium bromide and iodide, rather than sodium bromide and iodide, are the salts usually employed in making high-speed emulsions and that the alkali metal ion is never completely removed by the washing so that, regarding freedom from fog, there seems a lack of harmony between Campbell's observation and technical practice.

In an investigation "on the so-called Moser rays," Légrády³⁵ finds that aluminium and other metals high in the potential series are active in pure hydrogen, less active in nitrogen and still less active in air, the gases themselves showing no effect; and she concludes that not hydrogen peroxide but ionized hydrogen is the cause of the latent fogging. Dombrowsky discusses these results in his Dissertation, pp. 24-6, 29-33 (ref. 37).

Levin and Ruer³⁶ report that nine samples of potassium salts left for one hundred and ninety days separated from the emulsion film of Hauff plates by tissue paper and one thickness of black paper showed distinct activity, approximately equal to that shown by black uranium oxide in five hours.

Dombrowsky³⁷ publishes a thesis "on the action of various substances, especially hydrogen peroxide, on the photographic plate," the experimental part of which is mainly an investigation of the action of metals. The results seem to dispose of various objections that had been raised to Russell's view; but the mechanism of the latent fogging action of hydrogen peroxide as, *e.g.*, through chemiluminescence on decomposition, is not discussed, apart from allusion to the relatively slow reaction between hydrogen peroxide and silver bromide in gelatin.

³⁴ N. R. Campbell: *Chem. Zentralbl.* 78: II. 1047. 1907 (Sept. 25); from *Proc. Cambridge Phil. Soc.* 14: 211.

³⁵ E. Légrády: Über die sogenannten Moserstrahlen. *Z. wiss. Phot.* 6: 60. 1908 (Feb.).

³⁶ M. Levin and R. Ruer: Über die Einwirkung von Kaliumsalzen auf die photographische Platte. *Physik. Z.* 9: 248. 1908 (April 15).

³⁷ C. Dombrowsky: Inaugural Dissertation, Leipsic University. 1908.

Independently of Dombrowsky, Saeland³⁸ describes (1) experiments on the contact and distance action of emery-polished magnesium, aluminium, and zinc on a photographic film; (2) experiments similar to 1 but in hydrogen, dried air, or in partial or high vacua; (3) experiments on the question of the rectilinear spreading of the action between the metal and the photographic film, and the sweeping of the effect away by a current of air; (4) experiments on the destruction of the action by interposed diaphragms of brass or copper, and on the opacity to it of hole-free aluminium leaves. Saeland points out the general parallelism between these effects for high-potential metals and the effects for hydrogen peroxide solutions, and considers that the experiments prove the identity of the photographic action in the two cases.

In a paper "on the photographic activity of hydrogen peroxide and its supposed radioactivity," Dony and Dony³⁹ report a general parallelism between the vapor tension of hydrogen peroxide from its solutions and their activity. They conclude that the Russell theory adequately explains all the phenomena.

In a paper on "the action of resin and allied bodies on a photographic plate in the dark," Russell⁴⁰ shows that experiments with coal, peat, *etc.*, strongly indicate, as in the case of resin, that the action is produced by a vapor rather than by any form of radioactivity, and that the hydrogen peroxide explanation suggested in the case of metals and resin may also apply. Russell draws attention to the pronounced effect of a pre-exposure to white or blue light in increasing or creating activity in many substances, but offers no explanation of this.

Büch-Andersen⁴¹ finds that plates vary in sensitivity to metal rays, Agfa plates being most, and Lumière plates least sensitive. Büch-Andersen finds the brighter its surface the more active is an electro-positive metal, but with electro-negative metals the case is reversed.

In a paper "on the action of hydrogen peroxide, terpenes, resins, *etc.*, on the dry plate," Lüppo-Cramer⁴² gives an account of experiments tending to support his view that hydrogen peroxide acts not on the silver halide but on the silver present in highly dispersed form in emulsion films, converting it into a compound that produces latent fog as does silver nitrate.

³⁸ S. Saeland: Über die photographische Wirkung von Metallen und Wasserstoffsperoxyd (sogenannte Metallstrahlung). *Ann. Physik* **26**: 899. 1908 (Aug. 25).

³⁹ O. Dony and A. Dony: Über die photographische Wirksamkeit des Wasserstoffperoxyds und seine vermeintliche Radioaktivität. *Chem. Zentralbl.* **79**: II. 569. 1908 (Aug. 19).

⁴⁰ W. J. Russell: The Action of Resin and Allied Bodies on a Photographic Plate in the Dark. *Phot. J.* **48**: 345. 1908 (Nov.).

⁴¹ E. C. Büch-Andersen: *Eder's Jahrbuch* **23**: 342-3. 1909. From *Phys. Tidskrift* **7**: 7.

⁴² Lüppo-Cramer: Über die Wirkung des Wasserstoffsperoxyds sowie der Terpene, Harze usw. auf die Trockenplatte. *Eder's Jahrbuch* **23**: 102. 1909.

In a paper on the "action of ink on the photographic plate," de Fontenay⁴³ finds that the results obtained by Darget and attributed by him to life rays (*Comp. rend.* **147**: 1093) are due in part to the action of ink, and in part cannot be repeated. De Fontenay presumes that Darget omitted some necessary precautions.

In an article "on metal rays," Andersen⁴⁴ explains the activity of metals as due to intermediately-formed ozone, by assuming emission from oxidizing metal surfaces of a diffuse radiation of only slight penetrability and with the property of converting oxygen into ozone.

From experiments in which Seed plates were supported over a variety of salts of eighteen different metals for times ranging up to one hundred and sixty days, Strong⁴⁵ concludes that probably (only) erbium, potassium, and rubidium are radioactive.

In a paper "on pseudo-radioactive substances," Ebler⁴⁶ shows that the distance-action of zinc peroxide on Lumière plates is greatest with a fresh sample in a moist atmosphere, less pronounced with a some-weeks-old sample, and much less pronounced with a new sample in a desiccator. Basalt, which is rich in ferrous oxide, exhibits a distinct photographic action in moist air which disappears if the sample is heated to glowing and then tested in a vacuum.

Isitani⁴⁷ finds that scorching increases the activity of wood, and that the strongest results are obtained with an air space of a few tenths of a millimeter between the wood and the photographic film.

In a paper on "the action of organic peroxides on the photographic plate," Brooks⁴⁸ states that acetyl and other organic peroxides are very active, prolonged exposures giving reversal.

Vignolo-Lutati⁴⁹ observes that the action of resin on a photographic plate is arrested by the interposition of tin foil, vegetable membranes containing chlorophyll, quinone-soaked vellum, or thin disks of ordinary glass. The action of resin on a photographic plate is not arrested by Zeiss Uviol glass. Vignolo-Lutati supposes that the formation of ozone or

⁴³ G. de Fontenay: Action de l'encre sur la plaque photographique. *Comp. rend.* **148**: 112. 1909 (Jan. 11).

⁴⁴ E. B. Andersen (Erik Buch Andersen of Copenhagen, possibly identical with E. C. Büch-Andersen of ref. 41): Über Metallstrahlen. *Physik. Z.* **10**: 54. 1909 (Jan. 15).

⁴⁵ W. W. Strong: *Amer. Chem. J.* **42**: 147-50. 1909 (Aug.).

⁴⁶ E. Ebler: *Z. angew. Chem.* **22**: 1633-5. 1909 (Aug. 13).

⁴⁷ D. Isitani: *Physik. Z.* **10**: 1003-5. 1909 (Dec. 15).

⁴⁸ B. T. Brooks: The Action of Organic Peroxides on the Photographic Plate. *Chem. News* **101**: 40. 1910 (Jan. 28). From *Philippine J. of Sci.* **IV**: No. 5.

⁴⁹ F. Vignolo-Lutati: *Beibl. Ann. Physik* **37**: 1041. 1913 (Aug.). From *Atti di Torino* **14**: 363-76.

hydrogen peroxide in the aerial oxidation of resin is accompanied by emission of ultra-violet radiation which is the immediate fogging agent.

In the course of a paper on "some plate troubles: common and uncommon," Bloch⁵⁰ points out the danger of fogging due to the wood, aluminium or brass of plate-holders and slides, and also the necessity for care in the choice of paper for re-wrapping exposed and undeveloped plates and films. Bloch mentions that painting with potassium permanganate solution or melted paraffin wax will prevent the action of wood, and dilute platinic chloride solution will act similarly in the case of aluminium or brass. In renovating photographic apparatus "we should be careful what we use: all preparations containing linseed or other drying oils, turpentine and the resins and some of the fossil gums, are anathema."

In an article on catalyzers for the hydrogen peroxide reaction, Lüppo-Cramer⁵¹ describes experiments which lead to the recommendation to treat wrapping paper for plates by soaking it in a solution containing one per cent potassium permanganate and one per cent potassium or sodium carbonate, and drying before use. The permanganate is reduced to manganese dioxide, which remains on the paper fiber and prevents the liberation of hydrogen peroxide; and the carbonate protects against acid vapors. For protection against hydrogen sulfide also, Lüppo-Cramer recommends a further wrapping in paper that has been soaked in a one per cent solution of lead acetate.

In an article on "photechy," Lüppo-Cramer⁵² shows that resin-containing substances in general show an increase in activity by pre-exposure to light, and that this "photechic" effect is destroyed not only by permanganate, ferrous sulfate, potassium chromate, and all other catalyzers of the decomposition of hydrogen peroxide, but also by sodium hydroxide. The photechic effect is especially pronounced when plates color-sensitized with isocyanine dyes or with pinachrome are used. Lüppo-Cramer finds, however, that pure, (non-photechic) filter paper can not be rendered photechic by bathing it in solutions of pinachrome and pinacyanole.

He⁵³ points out that under darkroom conditions the sulfurous acid vapor of an acid-fixing bath, or even of a lead-gold p.-o.-p. toning-fixing bath, will fog a plate that is supported

⁵⁰ O. Bloch: *Phot. J.* 55: 220-2. 1915 (June).

⁵¹ Lüppo-Cramer: *Phot. Ind.* 14: 649-51. 1916 (Oct. 25).

⁵² Lüppo-Cramer: Über Photechie. *Phot. Ind.* 14: 713. 1916 (Nov. 22).

⁵³ Lüppo-Cramer: Über die schädliche Wirkung der schwefligen Säure in der Dunkelkammer. *Phot. Ind.* 14: 761. 1916 (Dec. 13).

inverted over the liquid, and that probably this vapor causes latent fog on stored plates.

Mace⁵⁴ publishes an illustrated article on "photochemical effects of a horse-shoe magnet," describing the effects obtained on ordinary plates (not further specified) by exposure in the dark in the field of a horse-shoe magnet. The editors of the *Brit. J. Phot.* comment that among the various checks upon the work mentioned in the article there is none "in which the various objects were left in contact with a sensitive plate, but not exposed to the alleged action of the magnetic field. A comparative test of this kind would have excluded an explanation of the effects on the ground of emanation action, which, as was shown by the late Dr. Russell, is the cause of many effects of this kind. Mr. Mace may have carried out such a check, but it is not clear from his text that he has done so."

In a paper "on the decay of the photochic reaction," Lüppo-Cramer⁵⁵ points out that an application of the starch-iodide test shows the formation of ozone or hydrogen peroxide on the surface of resin-containing substances such as wood and paper long after they have ceased to affect a photographic plate.

In a note on "experiments concerning 'magnet-photography,'" Bauer and Swann⁵⁶ state that a large number of experiments have been performed at the laboratory of the Department of Terrestrial Magnetism, Washington, D. C., some with permanent and some with electromagnets. "The details of these experiments are too numerous to be recorded in abstract, but it is concluded that while a magnetic field is not essential to the production of photographs of the kind cited [Mace's experiments, ref. 54], it probably has an influence in intensifying the effect."

In a note on "a new photographic phenomenon," McArthur and Stewart⁵⁷ give some details of an obscure printing effect which they have observed with a Meker or Bunsen flame or an electric kettle-heater through a plate box and a negative on to an otherwise unexposed Wellington Anti-Screen, Imperial Extra Rapid, or other plate.

In "some observations on the action of coal upon the photographic plate," Sinkinson⁵⁸ reports that the maximum effect

⁵⁴ F. F. Mace: Photochemical Effects of a Horse-Shoe Magnet. *Brit. J. Phot.* **63**: 678. 1916 (Dec. 15). From *Sci. Amer.*

⁵⁵ Lüppo-Cramer: Über das Abklingen der photoechischen Reaktion. *Koll.-Zeits.* **20**: 276. 1917 (June).

⁵⁶ L. A. Bauer and W. F. G. Swann: Experiments concerning "Magnet-Photography." *Phys. Rev.* **9**: 563. 1917.

⁵⁷ D. N. McArthur and A. W. Stewart: *J. Chem. Soc.* **115**: 973-4. 1919.

⁵⁸ E. Sinkinson: Some Observations on the Action of Coal upon a Photographic Plate. *J. Chem. Soc.* **117**: 165. 1920.

was found when undried coal was laid "in small heaps" on the film of an Ilford X-ray plate, without exclusion of air, and that no effect was observed in any case in an atmosphere of nitrogen.

Curtis⁵⁹ states that "working with a considerable number of dyes, a few were found which, under the conditions of the experiment, were not bleached to any great extent by either light alone or hydrogen peroxide alone, but which were bleached colorless after a few hours' exposure to light in the presence of hydrogen peroxide." He now shows that "the oxidizing power of hydrogen peroxide, as manifested in the bleaching of dyes, is increased by exposing the reaction mixture to light of short wave-lengths"; and that "this effect cannot be duplicated by substituting oxygen for hydrogen peroxide in the reaction mixture, indicating that the result is not due to formation of ozone."

Channon⁶⁰ describes some experiments on the prolonged action (up to two years) of zinc on latent light-images on photographic films.

Repeating experiments of Centnerszwer and Petrikaln, Jorissen⁶¹ finds that the action of phosphorus, in an aspiration apparatus, varies in the same way with the speed of the current of the air, as regards either a photographic plate or the ionization of the air.

In the course of an investigation of the size and sensitivity of grains in photographic emulsions, Svedberg⁶² finds that for very thinly re-coated plates and exposures to hydrogen peroxide vapor, the larger grains are the more sensitive.

Ebler⁶³ considers that the action of light on a photographic emulsion film may promote a process of aerial oxidation, which leads to the formation of minute amounts of hydrogen peroxide, and so of nuclei.

In a short paper "on the photogenic action of ultra-radiations," Nodon⁶⁴ states that the activity of uranium oxide or lead in contact with a photographic film in a light-tight box is increased by exposure to the sun or sky but not when exposed to the ground.

In an account of "some experiments on the action of wood

⁵⁹ H. A. Curtis: *J. Amer. Chem. Soc.* **42**: 720. 1920 (April).

⁶⁰ H. J. Channon: *Phot. J.* **60**: 167-70. 1920 (April).

⁶¹ W. P. Jorissen: L'action du phosphore, en voie d'oxydation, sur la plaque photographique et son pouvoir ionisant. *Rec. trav. chim.* **39**: 429. 1920.

⁶² T. Svedberg: *Z. wiss. Phot.* **20**: 36. 1920 (Aug.).

⁶³ E. Ebler: Über pseudoradioaktive Substanzen und Peroxyte. *Chem.-Ztg.* **45**: 59. 1921 (Jan. 15).

⁶⁴ A. Nodon: Sur l'action photogénique des ultraradiations. *Comp. rend.* **174**: 1061. 1922 (Apr. 18).

on photographic plates," Williamson⁶⁵ reports that the higher the temperature to which the wood has been submitted, the shorter is the necessary exposure time. The behavior of various woods is found to be in a certain measure characteristic, and an aid therefore in their botanical identification.

In an "introduction to a systematic determination of the cause of grey fog," Jacobsohn⁶⁶ alludes to the edge-fog that is usually seen in some degree on the development of stored plates. He distinguishes between the fog on original coating edges and the fog on the cut edges of smaller plates.

The following is an abstract of a paper by Rumpf⁶⁷ on "the 'Colson-Russell effect,' 'photochemical,' 'metal rays,' 'photo-activity' and other ray-like phenomena": "Many references are given to the work on the effect on a photographic plate of such substances as metals, hydrogen peroxide, fats and other organic substances. It is shown that the action of zinc on a photographic plate cannot be due to a wave radiation or to electrons, and Russell's conclusion is confirmed that the effect is due to a chemical reaction taking place on the surface, which may be oxidation by [*sic*] traces of hydrogen peroxide."

In an account of a "photographic method of deciphering charred documents," Davis⁶⁸ states that "it appears that the gases contained in the charred papers have the power to fog the photographic plate and that the ink acts as a screen hindering the escape of the gas. That is, on development, it is found that the plate has been blackened where it had been in contact with the charred paper except in those places occupied by the ink." Having found that slower plates, or papers, were comparatively insensitive, Davis used fast Seed plates.

Nodon⁶⁹ investigates the apparent increase in the action of radium on a sensitive emulsion when exposed with it in a light-tight box to the sun or sky. Interposed sheets of lead, card, mica, aluminium and celluloid tend to absorb the additional activity in the order named.

For the removal of latent edge and general fog from stored plates Milbauer and Flek⁷⁰ recommend bathing in 0.25 per cent hypo for fifteen minutes, then in one per cent potassium

⁶⁵ H. S. Williamson: Einige Versuche über die Wirkung von Holz auf photographische Platten. *Chem. Zentralbl.* 93: IV. 279. 1922 (July 19). From *Ann. Botany* 36: 91.

⁶⁶ K. Jacobsohn: Anleitung zur systematischen Ermittlung der Grauschleierursache. *Phot. Rund.* 60: 9. 1923 (Jan.).

⁶⁷ E. Rumpf: The "Colson-Russell Effect," "Photochemical," "Metal Rays," "Photo-Activity," and Other Ray-like Phenomena. *Phot. Abst.* 3: 131. 1923. From *Jahrb. Radioakt. Elektronik* 19: 214.

⁶⁸ R. Davis: Photographic Method of Deciphering Charred Documents. *Bur. Stand. Sci. Papers* 454. Reprinted in *Brit. J. Phot.* 70: 205. 1923.

⁶⁹ A. Nodon: *Comp. rend.* 176: 1705. 1923 (June 11).

⁷⁰ J. Milbauer and J. Flek: *Phot. Rund.* 61: 45. 1924.

persulfate for four minutes, washing and drying. It must be remarked that, without further knowledge, especially regarding the degree of development, this does not indicate any difference in the ease of destruction of latent storage fog as compared with the latent light-image.

Gerlach⁷¹ calls attention to certain articles by R. Eder, W. E. Pauli, and himself, that were overlooked in Rumpf's review (ref. 67). These showed that the observed effects on the photographic plate were the consequence of the chemical action of the vapors from the damp preparations, rather than of electro-magnetic or corpuscular radiation or of ionization.

In an investigation of "the photosensitivity of substances curative of rickets and the photolysis of the oxy-products by ultra-violet radiation," Kugelmass and McQuarrie⁷² conclude that "the data presented show that the substances curative of rickets, upon oxidation, blacken sensitive plates through quartz but not through glass screens. This phenomenon is undoubtedly due to the emission of ultra-violet radiation." But see ref. 77.

Clark⁷³ gives a semi-popular account of the latent fogging distance-action of resin, zinc, *etc.*, and also of the contact action of solutions of hydrogen peroxide, sodium arsenite, *etc.*, with the effect of pressure, all of which he terms "pseudo-photographic effects." He points out that many of the agents act like light in giving reversal with increasing time or intensity.

In a paper on the "action of fatty acids and oils on a photographic plate," Baughman and Jamieson⁷⁴ report that "heating to approximately 120° C. for several hours destroys or greatly decreases the activity. Blotting papers placed over very active oils become permeated with the active substance and capable of affecting a plate.

"The substance given off by an active oil will liberate iodine on a test paper saturated with a solution containing potassium iodide, starch, and a little ferrous sulfate. A paper saturated with titanium sulfate will be turned yellow by it, and one containing ferric ferricyanide will be turned blue, showing that there has been a reduction to ferric ferrocyanide.

"These results confirm Russell's opinion that the substance is hydrogen peroxide."

In an article "on latent fog," Lüppo-Cramer⁷⁵ states that even the intense fog produced by hydrogen peroxide, oil of

⁷¹ W. Gerlach: *Phot. Abst.* 5: 149. 1925. From *Jahrb. Radioakt. Elektronik* 20: 84.

⁷² I. N. Kugelmass and I. McQuarrie: *Science* 60: 272. 1924 (Sept.).

⁷³ W. Clark: Pseudo-Photographic Effects. *Sci. Progress* 19: 266. 1924 (Oct.).

⁷⁴ W. F. Baughman and G. S. Jamieson: Action of Fatty Acids and Oils on a Photographic Plate. *J. Frank. Inst.* 199: 416. 1925 (March).

⁷⁵ Lüppo-Cramer: Über den latenten Schleier. *Z. wiss. Phot.* 23: 184. 1925 (April).

turpentine vapor, *etc.*, on high-speed plates is completely removed by bathing the plate for a short time in a mixture of, *e.g.*, pinaflavol nitrate, ammonium bromide and acetic acid." All latent impressions on the plate which cannot be proved due to radiant energy but which are developable in the normal manner, Lüppo-Cramer defines as belonging to the domain of *secondary fog*. He then remarks that certain actions of this kind, such as that of hydrogen sulfide or phosphide, producing germs of silver sulfide or phosphide, which act like silver germs in inducing the separation of silver from its supersaturated solutions, are immediately intelligible. Concerning actions of hydrogen peroxide, ozone and terpenes, and the photochemical effect, there is a difference of opinion as to whether or not they are radiation phenomena. The author later reviews "edge-fog" briefly.

After describing their experiments on "the photochemistry of cod liver oil," West and Bishop⁷⁶ write: "In conclusion, though we have not perhaps demonstrated the absence of ultra-violet radiation from cod liver oil, all our positive findings of differential effects we have been able to trace to faulty procedure. Our results differ from those of Kugelmass and McQuarrie in that (1) we have been unable to confirm their positive findings, and (2) we have demonstrated the effectiveness of black body radiation in simulating such results, with poorly controlled technique."

Since their preliminary communication (ref. 72), Kugelmass and McQuarrie⁷⁷ write: "We have been forced to alter our original interpretation of the phenomenon observed." "The active agency in this phenomenon appears to be a material substance rather than a radiation, and chemical studies indicate that it is hydrogen peroxide, an intermediate product in organic oxidations."

Confirming previous workers, Harkins and Guy⁷⁸ obtain positive indications for the β -radioactivity of rubidium and potassium, the relative activity of which they observe to be as 1.39 : 1.

In a paper, of a preliminary nature, on the "evolution of hydrogen peroxide by oils on exposure to light," Stutz, Nelson, and Schmutz⁷⁹ concede that "the primary oxidation of an oil is probably a molecular autoxidation, where molecules of oxygen are added at the double linkings, thus forming peroxides.

⁷⁶ E. S. West and G. H. Bishop: *Science* **62**: 86. 1925 (July 24).

⁷⁷ I. N. Kugelmass and I. McQuarrie: *Science* **62**: 87. 1925 (July 24).

⁷⁸ W. D. Harkins and W. G. Guy: *Proc. Nat. Acad. Sci.* **11**: 628. 1925 (Oct. 15).

⁷⁹ G. F. A. Stutz, H. A. Nelson, and F. C. Schmutz: *Ind. Eng. Chem.* **17**: 1138. 1925 (Nov.).

Further action probably results in the breaking up of these peroxides with the evolution of hydrogen peroxide as well as other volatile products."

U. S. patent 1564707 is granted to V. M. Palmer and H. M. Thomas for a package of photographic material comprising a waterproof covering of layers of fabric and asphaltum which is substantially free from sulfur, ammonia, and turpentine.

In a paper on the photochemical action of some irradiated materials, Lucas⁸⁰ describes experiments in which pine sawdust, cholesterol, fur, skin, feathers, and wool, after exposure to the light of a quartz mercury lamp, were tested for fogging action on Eclipse Orthochromatic Superspeed plates. A strong effect was found with the pine sawdust and cholesterol, a doubtful effect with wool, and no effect with fur, skin, or feathers. Lucas concludes that the action "appears to be due to the production and subsequent gradual emanation of either hydrogen peroxide or ozone" and not to the emission of any secondary radiations capable of passing through a quartz plate.

Using plates coated with a pure bromide gelatin emulsion, Clark⁸¹ finds that the action of hydrogen peroxide vapor on the portion of a plate soaked in water immediately before exposure to the vapor is slower than that on the dry portion. The same effect is observed if an aqueous extract of potatoes (catalase) is used instead of pure water, although the former is an efficient catalyst for the decomposition of hydrogen peroxide, and this fact, with others, Clark concludes, "must be taken as evidence against the chemiluminescence hypothesis* and in favor of the purely chemical one."

From a review of the literature, Patton and Waldbauer⁸² conclude that rubidium and potassium salts emit heterogeneous β -rays, that no alkali metal emits detectable α -particles, and that sodium and lithium do not show any kind of radioactivity.

In the form of an article on "substances which affect photographic plates in the dark," Keenan⁸³ contributes an historical review somewhat similar to that of the present chapter, followed by a brief account of experimental work on the activity of various materials, mainly vegetable products. He finds

⁸⁰ N. S. Lucas: The Nature of the Action on a Photographic Plate of Sawdust and Cholesterol Irradiated by a Mercury Vapor Quartz Lamp. *Biochem. J.* **20**: 23. 1926.

⁸¹ W. Clark: *Phot. J.* **66**: 82-3. 1926 (Feb.).

⁸² I. J. Patton and L. J. Waldbauer: *Chem. Reviews* **3**: 81. 1926 (April).

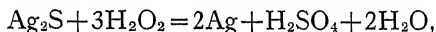
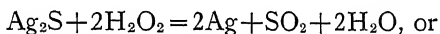
⁸³ G. L. Keenan: Substances which Affect Photographic Plates in the Dark. *Chem. Reviews* **3**: 95. 1926 (April).

*The suggestion that, by the decomposition of hydrogen peroxide, short-wave radiation is afforded at the surface of the silver halide grain, and particularly at photosensitive nuclei (Sheppard and Wigham, 1922).

"that an increase of temperature intensified the results obtained with various plant materials, such as sandalwood. Almost without exception, these are known to contain volatile aromatic principles, the evolution of which would be accelerated by heating." Keenan's historical review is valuable as supplementing that in the foregoing pages.

THEORY

The intermediate formation of hydrogen peroxide as an essential and characteristic step in the Vogel-Colson-Russell effect is supported by evidence which, although indirect, seems otherwise unusually satisfactory. In view of the extremely minute amount of hydrogen peroxide that suffices to produce latent fog on a photographic emulsion there does not appear at present to be any means of directly deciding the question. It should be noted that the reported passage of the active agent or agency through a vapor-impervious screen such as hole-free aluminium foil was not confirmed by later investigators. Assuming formation of hydrogen peroxide, it is necessary to consider the mechanism of the reaction by which it produces latent fog. Various suggestions have been offered, but none has met with general acceptance. The possibility of a reaction between silver sulfide* and *non-excess of* hydrogen peroxide giving rise to silver element and either sulfurous or sulfuric acid does not, however, appear to have been suggested. Such a reaction, represented by one of the equations:



is attended by the liberation of considerable energy; and it appears that the tendency of the silver element, first formed, to become oxidized and so disappear again as such is not great, provided that the hydrogen peroxide is always in deficiency of the silver sulfide.

*Shown by Sheppard to be, in all probability, the substance of the "sensitivity specks."

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